

PHOTOCHEMICAL CONVERSION OF SOLAR ENERGY

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Summary

A description is given of how solar chemistry could become a significant segment of the chemical industry and the basic concepts of photochemistry are reviewed. The three principal components of light (ultraviolet, visible and infrared) and their wavelength distribution have been described and typical solar spectra have been shown. The calculation of photonic fluxes from radiometric measurement and spectral data has also been introduced.

The attenuating components of the atmosphere and their effect on UV radiation have been discussed to achieve a final conclusion: UV spectrum is constant at a definite emplacement under certain circumstances. This characteristic permits the standardization of the solar-UV spectrum, which is very helpful for finding a standard photon flux and actinometric experiments have been shown to be useful to contrast the validity of all those equations related to photon flux calculation.

On-line measurement of UV power is essential and reactor efficiency must always be calculated considering, at least, the amount of energy incident on it. Very often, the use

of relative photonic efficiencies renders comparison of process effectiveness between studies carried out in different heterogeneous photocatalytic reactors possible.

1. Introduction

The dramatic increases in the cost of oil beginning in 1974 focused attention on the need to develop alternative sources of energy. It has long been recognized that the sunlight falling on the earth's surface is more than adequate to supply all the energy that human activity requires. The challenge is to collect and convert this dilute and intermittent energy to forms that are convenient and economical or to use solar photons in place of those from lamps. It must be kept in mind that today there is a clear worldwide consensus regarding the need for long-term replacement of fossil fuels, by other inexhaustible or renewable energies. Under these circumstances, the growth and development of solar chemical applications can be of special relevance. These technologies can be divided into two main groups:

- Thermochemical processes: the solar radiation is converted into thermal energy that causes a chemical reaction. Such a chemical reaction is produced by thermal energy obtained from the sun for the general purpose of substituting fossil fuels.
- Photochemical processes: solar photons are directly absorbed by reactants and/or a catalyst causing a reaction. This path leads to a chemical reaction produced by the energy of the sun's photons, for the general purpose of carrying out new processes.

It should be emphasized, as a general principle, that the first case is associated with processes that are feasible with fossil fuels. The second is related only to completely new processes or reactions that are presently carried out with electric arc lamps, fluorescent lamps or lasers. This contribution is focused on the second case: photochemical conversion of solar energy. Wide ranges of such chemical transformations have been proposed.

A few representative examples are given in Figure 1 to illustrate the concept. Norbornadiene is photochemically converted to a higher energy isomer and the energy can then be recovered by reversing the reaction shown in Figure 1(a). Photocatalytic processes have been intensively studied for producing hydrogen by splitting water as shown in Figure 1(b), or partially oxidizing hydrocarbons to produce oxygenated compounds as shown in Figure 1(c). Dye sensitized singlet oxygen reactions are being used to prepare 5-hydroxy-2,5-dihydrofuran-2-one from furfural as shown in Figure 1(d).

The sensitizer that is used is rose bengal, a dye that absorbs in the visible region of the solar spectrum. Photo-Fenton reaction has been introduced as a very promising water treatment method as shown in Figure 1(e). In the key reaction of the Photo-Fenton process Fe^{2+} ions are oxidized by H_2O_2 while one equivalent $\bullet\text{OH}$ is produced. The obtained Fe^{3+} or its complexes subsequently act as the light absorbing species that produce another radical while the initial Fe^{2+} is regained. These $\bullet\text{OH}$ radicals are highly reactive species (oxidation potential 2.80 V) can then be used to chemically decompose a pollutant into harmless end-products.

Because they are very technologically and environmentally attractive, solar chemical processes have seen spectacular development in recent years. The goal in this case is to provide a cost-effective and energy-saving source of light to drive photochemical reactions with useful products.

Therefore, the problem becomes one of identifying applications in which the use of solar photons is possible and economically feasible. The processes of interest here are photochemical hence some component of the reacting system must be capable of absorbing photons in the solar spectrum. Because photons can be treated like any other chemical reagent in the process, their number is a critical element in solar photochemistry. The need to know the amount of photons that enter in the reaction while in process is important, for a reactor using solar radiation, due to the following reasons:

- The radiation (sunlight) that reaches the reactor is not constant; therefore there must be a real time radiation measurement and precise knowledge of the spectrum that reaches the earth's surface.
- The extensive bibliography shows that the majority of the experiments in which the photon flux in the experimental system is known are illuminated by lamps.
- The quantum yields (ratio between absorbed photons and reacting molecules) of the reactions tested gives information on the optimum conditions of the process. Knowledge of the photon flux in this situation is fundamental for the determination of the efficiency of the components of the solar reactors and the possible modifications to be undertaken, in each case, to improve the conditions of the photochemical process.
- Any economic comparison between solar radiation and electric lamps requires knowledge of the photon flux incident on the solar reactor.

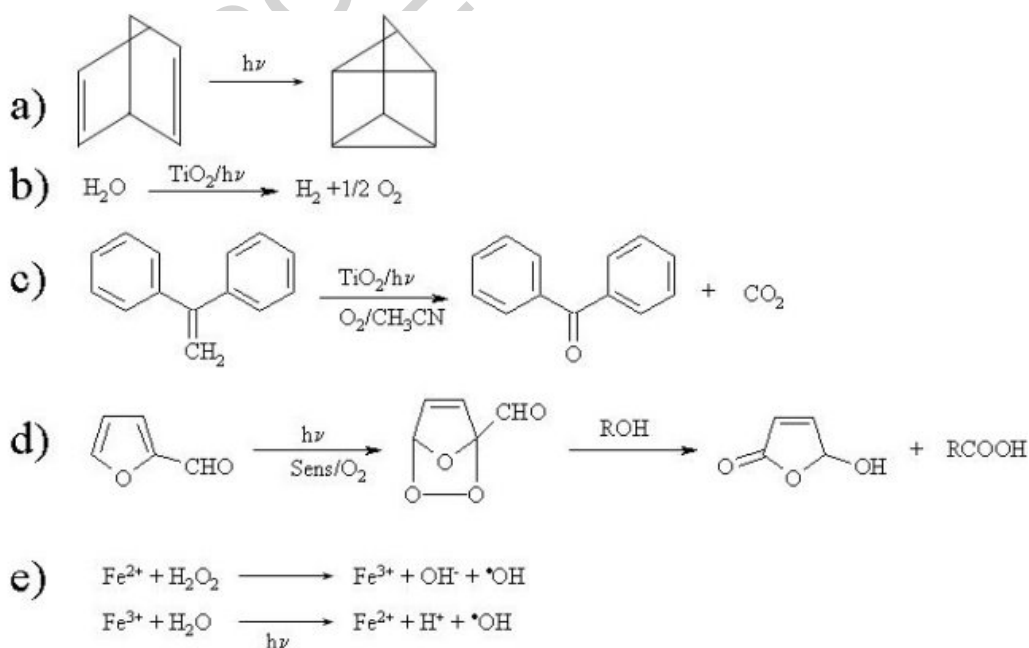


Figure 1. Representative examples of photochemical conversion of solar energy

Therefore, an overview of the principal parameters affecting the solar photon flux and the main experimental devices for its determination are presented in this chapter.

2. Photochemistry Principles

2.1. The Light

Light is just one of various electromagnetic forms of radiation energy present in space. The electromagnetic spectrum covers an extremely broad range, from radio wavelengths of a meter or more, down to x-rays with wavelengths of less than one billionth of a meter (see Figure 2). Optical radiation lies between radio waves and x-rays on that spectrum and has a unique combination of ray, wave, and quantum properties. At x-ray and shorter wavelengths, electromagnetic radiation tends to be quite particle-like in its behavior, whereas toward the long wavelength end of the spectrum behavior is mostly wavelike. Like all electromagnetic waves, light waves can interfere with each other, become directionally polarized, and bend slightly when passing through an edge. These properties allow light to be filtered by wavelength or amplified coherently as in a laser. In radiometry, light's propagating wave front is modeled as a ray traveling in a straight line (see Figure 2). Lenses and mirrors redirect these rays along predictable paths. Wave effects are insignificant in a large-scale optical system, because the light waves are randomly distributed and have plenty of photons.

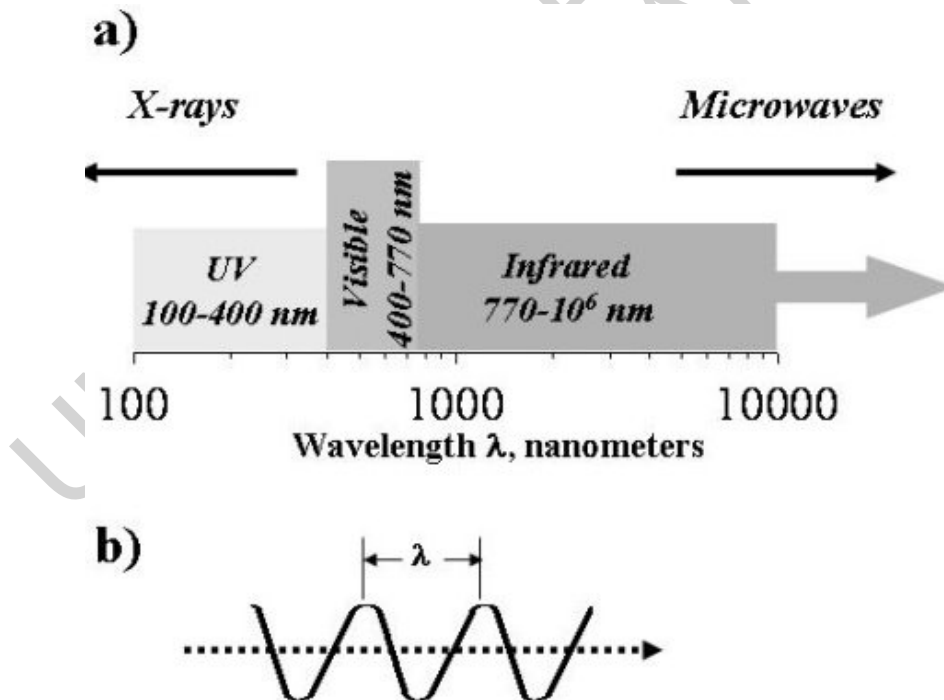


Figure 2. The optical portion of the electromagnetic spectrum (a) and light wave front modeled as a straight-line (b).

Short wavelength UV-light exhibits more quantum properties than its visible or infrared counterparts. This is the part of the solar spectrum more often used for photochemical applications because the UV photons are the most energetic of all arriving at the earth

surface. Ultraviolet light is arbitrarily broken down into three bands, according to its anecdotal effects. UV-A (315-400 nm), which is the least harmful type of UV light, because it has the least energy, is often called black light, and is used for its relative harmlessness and its ability to cause fluorescent materials to emit visible light – thus appearing to glow in the dark. UV-B (280-315 nm) is typically the most destructive form of UV light, because it has enough energy to damage biological tissues, yet not quite enough to be completely absorbed by the atmosphere. UV-B is known to cause skin cancer.

UV-C (100-280 nm) is almost completely absorbed in air within a few hundred meters. When UV-C photons collide with oxygen atoms, the energy exchange causes the formation of ozone. UV-C is never observed in nature, however, since it is absorbed so quickly. Germicidal UV-C lamps are often used to purify water because of their capability to kill bacteria.

Visible light is the radiation perceived by the human eye. Infrared light contains the least amount of energy per photon of any other band and is unique in that it has primarily wave properties. This can make it much more difficult to manipulate than ultraviolet and visible light.

Infrared radiation is more difficult to focus with lenses, refract with lenses, diffracts more, and is difficult to diffuse. Since infrared radiation is a form of heat, far infrared detectors are sensitive to environmental changes – such as a person moving in the field of view. Night vision equipment takes advantage of this effect, amplifying infrared radiation effect to distinguish people and machinery that are concealed in the darkness.

2.2. The Power of Light

In order for a photochemical reaction to take place, photons of light must be absorbed. The energy of a photon is given by Eq. (1).

$$U = \frac{hc}{\lambda} \quad (1)$$

where h is Planck's constant ($6.626 \cdot 10^{-34}$ J s), c is the speed of light and λ is the wavelength. For a molecule's bond to be broken, U must be greater than the energy of that bond. When a given wavelength λ of light enters a medium, its spectral irradiance E_λ ($\text{W m}^{-2} \text{ nm}^{-1}$) is attenuated according to the Lambert-Beer law, which is expressed in two ways, one for gas phase and the other for liquid phase:

$$\ln(E_\lambda^0 / E_\lambda^l) = \alpha_\lambda p_i l \text{ gas phase} \quad (2)$$

$$\log(E_\lambda^0 / E_\lambda^l) = \varepsilon_\lambda c_i l \text{ liquid phase} \quad (3)$$

E_λ^0 and E_λ^l are the incident spectral irradiances and at a distance l into the medium, respectively, α_λ is the absorption coefficient ($\text{cm}^{-1} \text{ atm}^{-1}$), p_i is the partial pressure (atm)

of component i , ε_λ is the extinction coefficient ($\text{M}^{-1} \text{cm}^{-1}$), and c_i is the concentration (M) of component i . The absorbance A_λ at wavelength λ is the product $\varepsilon_\lambda c_i l$.

The efficiency of a chemical reaction is calculated from the ratio between the products and the departing reactants. In photochemistry, it is very common to use the quantum yield concept, which is calculated from a known amount of photons absorbed in the reaction. Quantum yield (Φ) is defined as the ratio between the number of reacting molecules (Δn) and the quantity of photons absorbed by the system (N_a):

$$\Phi = \frac{\Delta n}{N_a} \quad (4)$$

Experimentally, the quantum yield is expressed as the number of moles of reactant transformed in an interval of time t , divided by the number of moles of photons absorbed during the same period. Knowledge of the quantum yield is rather important for an understanding of the mechanism of a photochemical reaction. If every absorbed photon produces a molecular transformation, $\Phi = 1$. If it is less than 1, it means that deactivation processes or other reactions competing with the one studied exist. Over 1 indicates a series of reactions the promoter of which has been excited by a photon. The number of photons absorbed by the system (N_a) is always related with the number of photons supplied by the source of light (N). In this case E^0 and E^l are substituted by N and N_a respectively in Eq. (2) or (3). When the light is produced by a monochromatic source of light with wavelength λ , the number of photons, N_λ , is related to the energy of one photon, U_λ , and the energy of the source of light energy, Q_λ , by Planck's equation (Eq. (5)):

$$N_\lambda = \frac{Q_\lambda}{U_\lambda} = Q_\lambda \frac{\lambda}{hc} \quad (5)$$

When a source of light is polychromatic as is solar radiation, the number of photons is given by an integral covering the whole range of wavelengths of that source:

$$N = \int_{\lambda_1}^{\lambda_2} N(\lambda) d\lambda = \frac{1}{hc} \int_{\lambda_1}^{\lambda_2} Q(\lambda) \lambda d\lambda \quad (6)$$

3. The Solar Spectrum

Radiation beyond the atmosphere has a wavelength of between 0.2 μm and 50 μm , which is reduced to between 0.3 μm and 4.0 μm when reaching the surface due to the absorption of part of it by different atmospheric components (mainly ozone, oxygen, carbon dioxide, aerosols, steam, clouds). The energy coming from that huge reactor, the sun is around 1.5×10^{18} kWh per year, or approximately 28000 times the world consumption for one year. The solar radiation that reaches the ground without being absorbed or scattered is called direct radiation; radiation that reaches the ground but has been dispersed is called diffuse radiation, and the sum of both is called global radiation.

In general, the direct component of global radiation on cloudy days is minimum and the diffuse component is maximum, while on clear days the opposite happens.

Figure 3 shows the standard solar radiation spectra at ground level on a clear day. The dotted line corresponds to the extraterrestrial radiation in the same wavelength interval. When this radiation enters the atmosphere, it is absorbed and scattered by atmospheric components, such as air molecules, aerosols, water vapor, liquid water droplets and clouds. The spectral irradiance data are for the sun at a solar zenith angle of 48.19° . This zenith angle corresponds to an air mass of 1.5, which is the ratio of the direct-beam solar-irradiance path length through the atmosphere at a solar zenith angle of 48.19° to the path length when the sun is in a vertical position.

The air mass is equal to 1 when the sun is directly overhead (zenith). As air mass increases, the direct beam traverses longer path lengths in the atmosphere, which results in more scattering and absorption of the direct beam and a lower percentage of direct-to-total radiation (for the same atmospheric conditions). The radiation effectively reaching the ground level varies strongly due to several factors, such as geographic latitude, date, time of day, atmospheric conditions (aerosols, humidity, etc.) or simply cloudiness. Figure 4 shows the global UV irradiance measured at Plataforma Solar de Almería on a plane tilted 37° on cloudless days in different seasons. To judge the feasibility and profitability of a solar application at a specific site, studies have to be performed to measure or estimate the amount of radiation actually available at the site in question along the year. Due to the large variability of radiation conditions from year to year such studies have to be based on data collected from at least five years to be considered statistically significant.

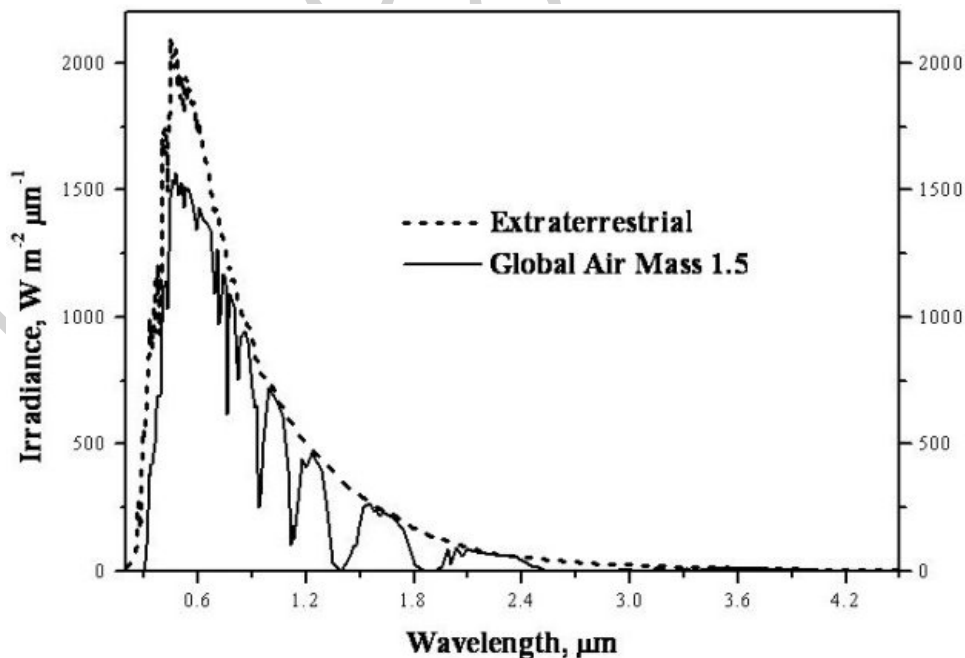


Figure 3. Spectral solar radiation plotted from 0.2 to 4.5 μm .

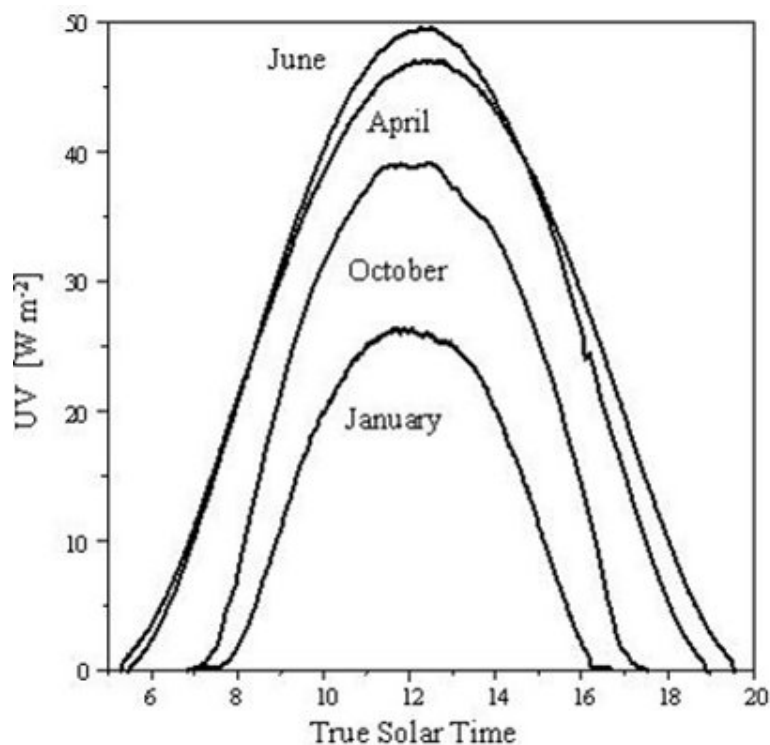


Figure 4. UV irradiance during a typical cloudless day at Plataforma Solar de Almería on plane tilted 37°.

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Biographical Sketches

Sixto Malato. Born in Almería (Spain) on 10th May, 1964. Dipl. Chemistry (Chemical Engineering) by Facultad de Ciencias of University of Granada (1987). Master in Environmental Sciences by the Instituto de Investigaciones Ecológicas (Málaga, 1994). PhD in Chemical Engineering at the University of Almería (1997). 18 years of experience having worked at different sectors.

His professional activities started in 1987 as Junior Researcher in Chem. Eng. Department of Univ. of Almería; in 1988 he joined the Production Department in an oil refinery (REPSOL S.A.) in Puertollano (Spain). Since 1990 he works at the Plataforma Solar de Almería (PSA-CIEMAT) in all the EU R&D projects linked to the Solar Detoxification of water. Concretely, he has been involved in 11 EU, 13 National R&D Projects and 6 R&D Contracts (with Private Companies) related to the development of solar wastewater treatment technologies, and has been involved in the design and construction of all the experimental pilot plants for solar detoxification of industrial waste water in Europe. He author of 1 book and co-author of 5 books as well as 21 chapters in others. He has also co-authored more than 80 publications in indexed international journals, 21 articles in technical journals and more than 140 contributions to 68 different International Congress and Symposiums and 4 patents. He has attended 31 Workshops and Conferences on Water Treatment and participated as a teacher in 17 courses on Advanced Wastewater Treatment. He has directed 4 PhD dissertations. The Jury's Grand Prix of "European Grand Prix for Innovation Awards" (Monaco, December 2004)

Julian Blanco Gálvez. Born in Almería (Spain) on 16th August, 1960. Dipl. Industrial Engineer by the *Escuela Superior de Ingenieros* (Seville, 1984), Master in Environmental Sciences by the *Instituto de Investigaciones Ecológicas* (Málaga, 1994); PhD by the *University of Almería* (2002). Dept. of Applied Physic.

His professional activities started in 1985 as head of production department (COEMTER, Gerona, Spain), 1985-1988; Product Engineer (AMP Corporated, Barcelona, Spain), 1988-1990; working on the research field to CIEMAT since 1990, at Plataforma Solar de Almería. At present he has a permanent position as Senior Researcher of the Spanish Ministry of Education and Science. In 1995 he become the head of the CIEMAT "Solar Chemistry" area at PSA and, in 2002, the head of the "Environmental Applications of Solar Energy" department of CIEMAT. Spanish National Representative in the Task II IEA-SolarPACES since 1995. During the last 16 years he has been fully involved into research activities related with the application of solar energy to water processes (detoxification, disinfection and desalination) and applications with the main objective on innovative technology development. He has been involved in 16 European Union projects (7 of them as leader/coordinator), 15 National R&D Projects and 6 R&D Contracts (with Private Companies) all of the related with the development of Solar processes and technologies. Author of 4 patents, author/co-author of 7 full books, and 18 chapters in different books; he also has more than 50 publications in indexed international journals and more than 135 contributions to

about 75 different International Congress and Symposiums. He has given multiple invited lectures in courses, conferences and seminars all over the world collaborating with institutions such as UNITED NATIONS and EURESCO in specific project and activities related with technology diffusion and human resources formation. He received the Jury's award of the "European Grand Prix for Innovation Awards" (2004).

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