

Review

Abiogenesis and photostimulated heterogeneous reactions in the interstellar medium and on primitive earth Relevance to the genesis of life

A.V. Emeline^a, V.A. Otroshchenko^{b,1}, V.K. Ryabchuk^c, N. Serpone^{a,*}

^a Department of Chemistry and Biochemistry, Concordia University, 1455 deMaisonneuve Blvd. West, Montreal, Que., Canada H3G 1M8

^b Bakh Institute of Biochemistry, Russian Academy of Science, Moscow, Russia

^c Department of Photonics, Institute of Physics, St-Petersburg State University, Saint Petersburg, Russia

Accepted 29 October 2002

Abstract

Heterogeneous reactions occur on solid photocatalyst particles of semiconductors and dielectric materials. When irradiated with suitable UV/visible light energy these particles generate electrons and holes, which on the surface are poised to undergo reductive and oxidative chemistry with a variety of organics and light gases. Various such particles have been identified in Interstellar Space, specifically in molecular–dust clouds, comets and meteorites. In this article, we examine briefly the nature of these dust clouds and then describe some basic aspects of heterogeneous photocatalysis, a methodology that has been shown useful in transforming organic substrates into smaller molecules and in the synthesis of potential biomolecules. Various types of gas/solid heterogeneous reactions involving mostly small molecules in gas/solid systems find a relationship to abiogenesis. For example, the decomposition of H₂O and CO₂ in the presence of CH₄ yields H₂CO; methane is photoconverted into ethane, propane, ethylene and other hydrocarbons and is photooxidized to alcohols and carbon dioxide; photofixation of CO₂ occurs to yield formaldehyde, formic acid, methanol and methane; and finally photofixation of molecular nitrogen N₂ can take place to produce NH₃ and N₂H₂. Not least is the synthesis of glycine, alanine, aspartic acid and serine from CH₄ and NH₃ over platinized titania. The relevance of heterogeneous photocatalysis to abiogenesis is discussed. It is argued that the physical conditions available in the interstellar medium are propitious to generate such biomolecules as amino acids and others, albeit this assertion necessitates laboratory simulations. Recent laboratory experiments involving very simple photoinduced processes are encouraging.

© 2002 Japanese Photochemistry Association. Published by Elsevier Science B.V. All rights reserved.

Keywords: Interstellar space; Heterogeneous photocatalysis; Abiogenesis; Interstellar medium; Genesis of life

Contents

1. Introduction	204
2. Interstellar molecular–dust clouds	206
3. Heterogeneous photocatalysis and related phenomena	208
4. Solid photocatalysts and photocatalyzed reactions	214
4.1. Decomposition of water and carbon dioxide	215
4.2. Photoconversion of methane	215
4.3. Photofixation of CO ₂	216
4.4. Photofixation of molecular nitrogen	216
4.5. Addition of amino acids and peptides	216
5. Additional features of heterogeneous photoreactions	216
5.1. Dependence of kinetics on light intensity and pressure	216
5.2. Temperature dependence	217

* Corresponding author. Fax: +1-514-848-2868.

E-mail addresses: vladotr@inbi.ras.ru (V.A. Otroshchenko), ryabchuk@photonics.phys.spbu.ru (V.K. Ryabchuk), serpone@vax2.concordia.ca (N. Serpone).

¹ Fax: +7-95-954-27-32.

5.3. Process efficiencies	217
5.4. Spectral selectivity	219
6. Relevance of heterogeneous photochemical reactions to interstellar abiogenesis—issues and perspectives	219
Acknowledgements	221
References	221

1. Introduction

Several millenia of chemical evolution had passed before the first living organisms (protobionts) appeared on earth some 3–3.5 billion years ago. Whatever the location of abiogenesis on primitive earth and/or in the interstellar medium, (ISM), pre-biotic molecules were created from simpler precursors, namely atoms and molecules. After the pioneering experiments of Miller and Urey in the mid-20th century, and subsequent to the experimental studies by Miller and coworkers [1,2] and by Fox and Dose [3], it became evident that *in vitro* mixtures of simple molecules could be generated under conditions that simulated the primitive atmosphere on earth. Various pre-biotic organic molecules can be produced under the actinic effect of charged particles, UV photons, γ -rays and X-rays among others. The impressive expansion of radio, infrared, and other spectroscopic and instrumental methods in astronomy in the last three decades has led to the identification of more than one hundred molecules, including organic substances containing up to 13 carbon atoms in the interstellar medium mostly by means of infrared space observation (ISO) techniques and radio-astronomy methods [4]. Identification of new molecules of this kind continues to be a topic of active investigation (see also [5]).

Cosmic dust clouds of different types (see, e.g. Fig. 1a–d) are considered as the main ISM sites at which molecules are produced. According to the current level of understanding, primitive life started on earth only after ~ 700 million years had passed since the end of the heavy bombardment phase of earth's formation (see, e.g. [6,7]). Contrary to earlier views, the early earth's atmosphere was probably strongly reductive and consisted principally of CO_2 , N_2 , and H_2O . Accordingly, life was likely created on earth as the result of a very short-time scale abiogenesis. This discordance and the discovery of a large number of organic molecules in interstellar space [5] has brought new insights to the problem of *panspermia*, i.e. to the problem of the extraterrestrial origin of life, one of the key issues in astrobiology. It appears that the first “building blocks” of the genesis of life were brought to earth by meteorites, micrometeorites, comets and other celestial bodies. Dust, comets, and other bodies are the oldest inhabitants in the earth's environment. The components of interstellar dust clouds gave birth to our solar system some 5 billion years ago.

The primitive and modern earth atmospheres, oceans and land (or more generally known as the biosphere) of the last 3–3.5 billion years, and molecular–dust clouds in the ISM

space are natural open non-equilibrium systems that absorb free energy of different types and from different sources [3,8,9]. Solar UV radiation was likely the most powerful source of free energy to drive the complex abiogenic processes on the primitive earth relative to other free energy sources. For example, the fractions of UV light energy and other energy sources normalized to the total solar radiation are estimated to be ca. 2.2×10^{-3} at wavelengths (λ) shorter than 250 nm, 3.4×10^{-5} at λ below 200 nm, 1.35×10^{-5} below 150 nm), 1.54×10^{-5} from electric discharges and lightning, 3×10^{-6} from natural radioactivity of the earth's crust and lower sublayers, 5×10^{-8} from volcanoes and 6×10^{-9} from cosmic rays [10]. The contribution to the total free energy of the abiogenic process from shock waves arising from penetration of meteorites into the earth's atmosphere has also been treated [11]. The role of cold ionospheric plasma in abiogenesis on earth has been proposed and considered by Simionesku and Denes [12].

The atmospheres of primitive and modern earth are in reality heterogeneous systems since they include solid dust, aerosol particles, and water droplets (water/air interface, clouds). They possess principal interfacial boundaries both with the lithosphere and the hydrosphere. The same is true in relation to what is referred to as the lithosphere and the hydrosphere. In general then, one must consider the field of the origin of life on earth as a rather complex heterogeneous system. The widely discussed heterogeneity of the system has been considered at the different stages of the multi-step process of the origin of life in many studies and theories [13]. The exchange of gaseous species between the lithosphere and mantle (including volcanic gases) and between the atmosphere and atmospheric gases, including the products from the various atmospheric thermal and photochemical reactions and from the water phase (i.e. oceans), as well the role of various heterogeneous catalytic reactions, have been treated in studies of the chemistry in primeval and present-day earth. The latter field is now known as geocatalysis [14]. Similarly, the heterogeneity of dust clouds and of catalytic processes with dust particles is under extensive theoretical investigations and experimental modeling [6,15–17]. The role of UV radiation in the chemistry of interstellar dust has been discussed by Gerakines et al. [18].

In the early studies, the primitive earth's atmosphere was treated principally as a gaseous homogeneous system in relation to photochemical processes driven by the direct action of solar radiation. In actual fact, the red limits of the spectral regions (see above) for which estimates of solar

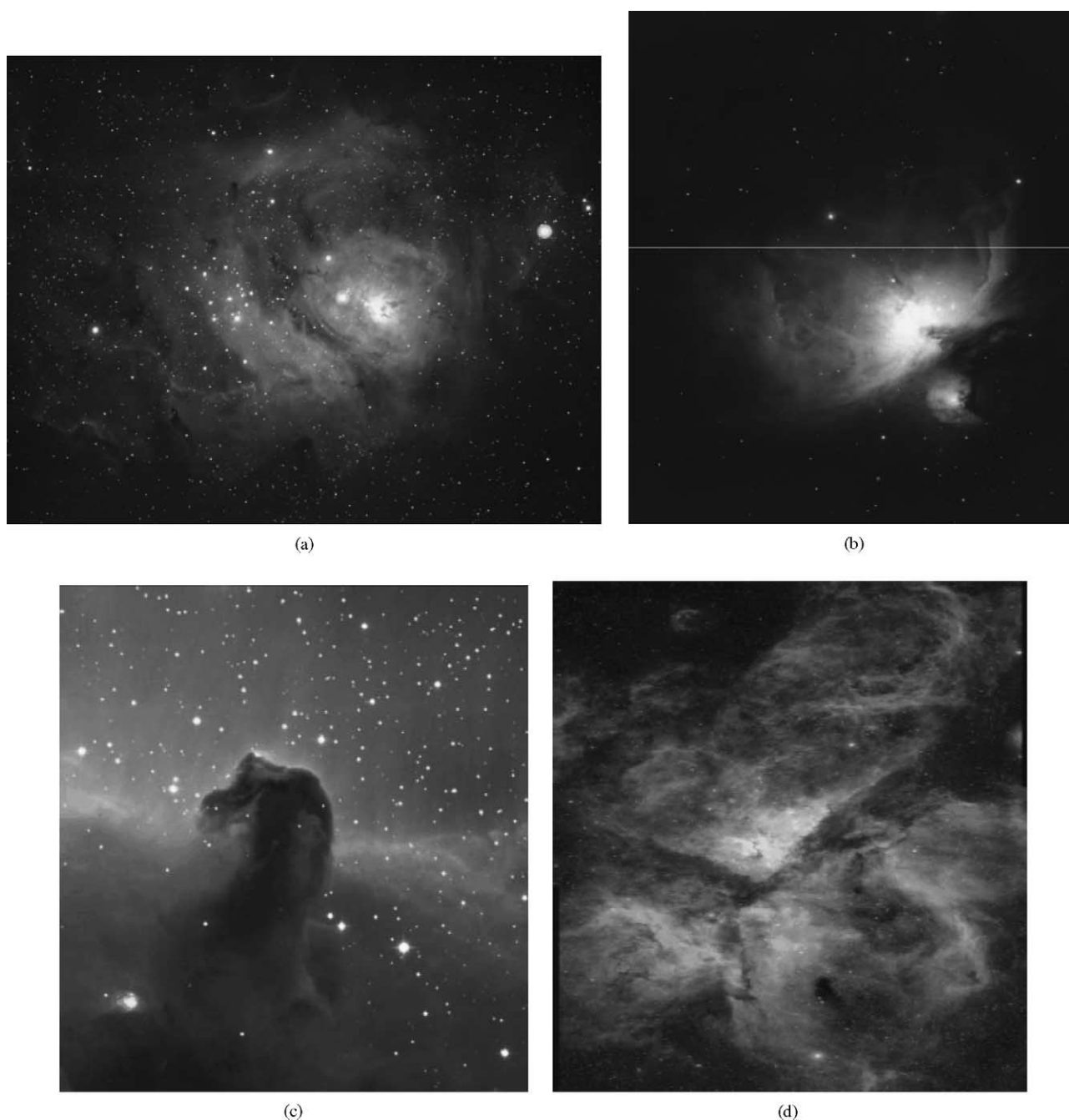


Fig. 1. (a) The Lagoon Nebula in the constellation Sagittarius glowing with the light of H (alpha) excited by the radiation of very hot stars buried within its center. Dark filaments of obscuring matter emit strong IR radiation. (Copyright the National Optical Astronomy Observatory/Association of Universities for Research in Astronomy and funded by the National Science Foundation, 1973). (b) The Orion Nebula in the constellation of Orion the Hunter. It is composed mostly of neutral and ionized hydrogen (H^+ ions) responsible for the glow—the ions recombine with electrons. It also contains significant quantities of oxygen. (Copyright Bill Schoening, the National Optical Astronomy Observatory, the Association of Universities for Research in Astronomy, and funded by the National Science Foundation, 1976). (c) The Horsehead Nebula also in the constellation of Orion. It is an extremely dense cloud projecting in front of the glow. (Copyright N.A. Sharp and, the National Optical Astronomy Observatory, the Association of Universities for Research in Astronomy, and funded by the National Science Foundation, December 1994). (d) The Carina Nebula illustrates how very massive stars rip apart the molecular clouds that give birth to stars. It consists of oxygen (relatively hot region), hydrogen and sulfur (relatively cooler region). (Copyright Nathan Smith, the University of Minnesota, the National Optical Astronomy Observatory, the Association of Universities for Research in Astronomy, and funded by the National Science Foundation).

irradiance have been done correspond to the red limits of the direct photolysis of free NH_3 (225 nm), water (185 nm), CO and CH_4 (ca. 150 nm). In studies of the photochemistry of interstellar dust particles, the photoexcitation of molecules frozen in so-called icy mantles of dust particles (see below) is typically considered as the first step of the reaction sequence. Herein, we entertain other possible pathways of heterogeneous photoreactions both for the interstellar and atmospheric dust in view of the many published studies on heterogeneous photocatalysis and related phenomena [19–21].

To our knowledge, Terenin [22] was the first to point out, however briefly some four decades ago, the possible role of heterogeneous photocatalysis and related phenomena in the abiogenesis on primitive earth. Solar UV radiation was considered the most powerful source of free energy relative to others (see above). He emphasized the effect of “red shifts” of spectral ranges of photochemical reactions in gas/solid heterogeneous systems arising from adsorption. These red shifts could lead to a more effective involvement of long wavelength solar radiation in abiogenic syntheses compared to the short-wavelength radiation typically used in the photochemistry of free molecules. In line with abiogenesis occurring on primitive earth, exobiological aspects of heterogeneous photochemical reactions have been considered in a few reports. These studies were inspired partly as a result of the first pilotless mission to Mars and search for the footprints of life on this planet. Chun et al. [23] have described the positive (i.e. synthesis of organics in model experiments in gas/solid heterogeneous systems under actinic UV light; see, e.g. [24]) and the negative role (oxidation of organics on TiO_2 particles on the Martian surface) of trace atmospheric oxygen in the abiogenic processes taking place on Mars.

Studies of heterogeneous photocatalysis by several workers (see, e.g. [19–21] and references therein—the original studies will be described in more detail below) demonstrated the potential for the synthesis of various biologically important molecules from simple precursors. The large body of data presently available permits a discussion of the possible role of heterogeneous photochemistry in abiogenesis both on primeval earth and in the interstellar medium, ISM. In addition, the variety and high efficiency of heterogeneous photochemical processes in modern earth’s atmosphere reported in recent studies [25–27] infer that similar processes must also have been significant on the primitive earth, notwithstanding the fact that physical conditions and the chemical composition of the primitive earth’s atmosphere differed dramatically from the modern earth’s atmosphere.

In this article, we discuss interstellar natural abiogenesis in terms of photochemical reactions that take place in gas/solid heterogeneous systems. After a brief description of interstellar dust properties, the principles of heterogeneous photochemistry are also described. Laboratory studies of the photocatalytic transformation of molecules that might have occurred in the early earth’s atmosphere and in interstellar dust clouds, together with the properties of potential solid catalyst particles that might have existed

in the earth’s atmosphere and in the ISM, will also be discussed briefly. Special features of heterogeneous photoreactions in gas/dust cloud systems (both in planetary atmospheres and in the ISM) that might be favorable to abiogenic syntheses are emphasized.

2. Interstellar molecular–dust clouds

Single stars, binary stars, and stars associated into groups of various levels of complexity up to galaxies and higher make up the universe. Their total mass appears to be less than (0.7–0.8) that of our Milky Way spiral galaxy (henceforth, Galaxy). The mass fraction of stars is less for irregular galaxies such as, for example, Magellanic Clouds, and is greater for elliptic and spherical galaxies. The rest of the mass belongs to gases and dust occupying interstellar space and forms through the action of photons, cosmic rays, electromagnetic fields and others, in the so-called interstellar medium. Both molecular and atomic hydrogen and helium account for nearly all the mass of interstellar gas. About 0.001 of the ISM mass belongs to the heavier (“metallic”) elements such as C, N, O, and others. In turn, nearly 0.01–0.03 mass fraction of the ISM in the Galaxy is referred to as “dust”, i.e. solid particles of micron and submicron size. Interstellar dust plays many important roles. Dust and gas form the so-called interstellar clouds with a more or less definite spatial distribution of gas and dust densities. Gas/dust clouds generally differ in the relative content of atomic and molecular hydrogen, in gas density, in size and other properties. The temperatures and densities of hydrogen $n(\text{H})$ of different types of interstellar clouds are summarized in Table 1 [28].

Giant molecular clouds [very rarefied, hot, $T \approx 10^6$ K, ($n(\text{H}) \approx 0.003 \text{ cm}^{-3}$)], occupying very large volumes and arising from supernova explosions, have been identified. Spaans and Ehrenfreund [15] have provided a detailed classification of interstellar clouds. Dust clouds are observed as they evolve, and the same is true of stars and other space objects. In particular, dense dark clouds form from diffuse ones (see Fig. 1a–d).

Generally, interstellar clouds consist of both gas and dust. The dust plays an important role in the thermal balance of the ISM. Stimulated by UV photons, the emission of electrons from dust particles and their subsequent inelastic collisions with hydrogen in a gas contributes to the thermal equilibrium of the ISM (photoelectric heating). By contrast, dust particles are warmed by irradiation from the stars and

Table 1
Temperature of and hydrogen density in interstellar dust clouds [28]

	Cloud types			
	Diffuse clouds	Dark clouds	Molecular clouds	Globulae
T (K)	10^2 – 10^3	10 – 10^2	5–50	10–30
$n(\text{H})$ (cm^{-3})	1 – 10^2	10^2 – 10^4	400 – 10^6	10^2 – 10^5

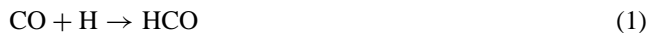
by hot electrons (in hot clouds) and are cooled by emission of photons mainly in the infrared (IR) and far-infrared (FIR) regions. Dust, whose mass fraction is 0.0003, has a total luminosity of a fraction around 0.4 of the luminosity of stars in the Galaxy [28]. With increasing cloud density, the fraction of molecular hydrogen increases as a result of changes in the balance between dissociation of molecular hydrogen by UV photons and recombination of hydrogen atoms catalyzed by dust particles. The neutrality of the ISM media also increases with increasing cloud density owing to screening of short wavelength radiation from stars, which causes photoionization of atoms and molecules.

Interstellar dense clouds contain the raw materials (dust and molecules), which are the building blocks in the formation of stars [29]. The final event of dust cloud evolution is the birth of a star, which ranks as the main sequence in the RH (Ressel–Hertzsprung) diagram in accordance with its mass. The remnants of interstellar dust clouds may be present in planetary and stellar environments. The principal sources of interstellar dust in the Galaxy are the atmospheres of red giants, in which dust particles evolve and devolve by star irradiation and novae and supernovae explosions. On expansion into space, molecular–dust clouds cool and disperse. Then, because of gravity and various other effects, clouds begin to compress, a process that can lead to the birth of new stars [28].

Two main types of dust grains are carbonaceous and silicate (e.g. magnesium and iron silicates such as olivine, orthopyroxene, and forsterite) in origin. The carbonaceous dust originates in stars' envelopes when the C/O ratio is greater than unity. In this case, silicate and oxide grains do not form because of C and O coupling in CO. By contrast, silicate and metal-oxide grains form at C/O ratios less than unity. The C/O ratio is determined by the nature of the stars in whose environments nuclei of heavy elements are produced. Some small molecules, such as CO, as well as fullerenes, polyaromatic hydrocarbons (PAH) and other carbon-based species (see for example [7]) can also be produced directly close to the stars. However, complex molecules are produced at the surfaces of dust clouds. Relatively simple molecules such as H₂, HD, CH, OH, NH, C₂, CO, CN, and CS have been found in rarefied diffuse clouds. The majority of more complex molecules have been observed in dense, relatively cold clouds. It will be useful to describe a few salient points of the astrochemistry of dust clouds.

The dust grains in cold clouds ($T < 100$ K) serve as sites of condensation of molecules, with the exception of hydrogen and helium. Dust grains are typically covered by an icy mantle, which consists mainly of water ice with incorporated molecules. Polar and apolar ices can be distinguished. Polar ices form in media that contain hydrogen and consist of incorporated CO, CO₂, CH₄, NH₃, CH₃OH (and other minor species), whereas apolar ices form in hydrogen-poor media and include more volatile components such as CO, N₂, O₂ and CO₂. The synthesis of molecules at the surface of dust particles and icy mantles can occur even at extremely low

temperatures through reactions that involve hydrogen atom addition, beginning with the reaction between a hydrogen atom and CO [30], Eqs. (1)–(3):



Note that H atoms exist in significant amounts in interstellar gas and remain mobile in ices even at very low temperatures; CO is the second-most abundant molecule in Interstellar Space. Formation of a whole set of organic compounds detected in dense clouds likely involves thermal and energetic cosmic rays [31–33], shock waves arising from novae and supernovae explosions [11], high velocity dust/dust collisions [34,35] and UV photons. It is relevant to emphasize that an internal source of UV photons exists even in the inner part of dense dark clouds. As noted by Prasad and Tarafdar [36], the highly penetrating cosmic rays cause excitation of H₂. The radiation decay (luminescence) of excited molecules produces a UV flux of $I \approx 1000$ photons $\text{cm}^{-2} \text{s}^{-1}$ at $E(h\nu) \geq 6$ eV. Laboratory simulations of UV processes in different pure ices [18] with a UV light flux of $I \approx 10^{15}$ photons $\text{cm}^{-2} \text{s}^{-1}$ revealed formation of radicals and complex products for exposure periods corresponding to characteristic lifetimes (or shorter) of dense clouds. On increasing the temperature, molecules and radicals produced on icy mantles at very low temperatures undergo further transformations and desorb during the sublimation of mantles in the course of cloud evolution to a proto-star and further. Hence, interstellar dust particles exist under a very wide range of physical conditions. Clearly, photo-processes can occur on dust particles even in dense dark clouds. Consequently, a priori it is reasonable to expect that heterogeneous photochemical reactions may also occur at the interfaces of mineral grain/icy mantles, mantles/gas in cold media, and grain/gas in relatively hot regions.

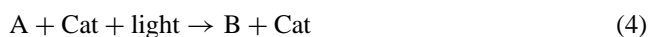
In stars' planetary systems, in particular in the solar system, the variety of physical conditions in dust clouds may be even more diverse. Indeed, the chemical compositions of molecules and their abundance in cold dense clouds are very close to those in comets. Although the presence of the amino acid glycine in dark clouds has not yet been confirmed, more than 10 amino acids have been found in carbonaceous chondrites [37]. This calls attention to the notion that complex pre-biotic compounds may be generated during the last stages of dust cloud evolution from diffuse clouds, through to formation of dense clouds and ultimately planets. Accordingly, during such evolution, including the evolution of earth and earth's atmosphere in their early stage on the way to the origin of life, we can envision conditions of large photon fluxes in the UV and visible range, high gas pressures and moderate temperatures.

Heterogeneous photochemical reactions are being examined in many laboratories under similar experimental conditions. The mechanisms by which such reactions occur

are reasonably well understood. It is instructive, therefore, to describe some of the salient features of heterogeneous photocatalysis and some properties of semiconductors and dielectric insulators that act as the photocatalysts, to call attention to possible similarities with what transpires in pre-biotic chemistry in the ISM.

3. Heterogeneous photocatalysis and related phenomena

Heterogeneous photocatalysis has been established as a common and widespread technology having its origins focused mostly on environmental remediation and detoxification [19,20,38]. In brief, heterogeneous photocatalysis (HPC) is best simplified by Eq. (4), [39]:

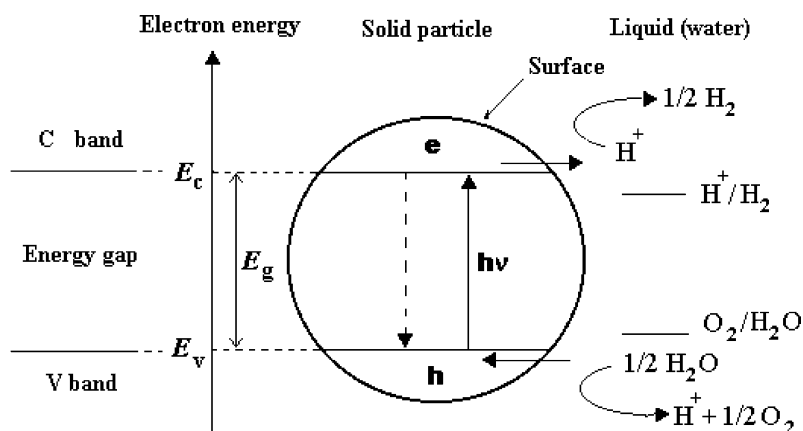


where A and B are chemical reagents and products, respectively, in the gaseous or liquid phase, and Cat denotes the solid photocatalyst. Where reagents (A), products (B) and catalyst (Cat) are in the same phase (typically gaseous or liquid), reaction 4 then describes homogeneous photocatalysis. Thus, HPC is the generalization of the non-catalytic chemical reaction ($A \rightarrow B$), thermal heterogeneous catalysis (acceleration of the reaction rate with conservation of the catalyst Cat: $A + \text{Cat} \rightarrow B + \text{Cat}$), and photochemistry (involvement of free energy in the process $A + \text{light} \rightarrow B$). Heterogeneous photocatalysis can also be treated as a special case of biological photosynthesis. The latter includes the self-reproduction of the photosynthetic system (Cat), whereas in photocatalysis it is the reactivation of Cat during a sufficiently high number of catalytic cycles. When the catalytic cycle in reaction 4 is not complete (i.e. Cat is not restored), the process is then a simple heterogeneous photochemical reaction (HPR).

The general process of Eq. (4) can be achieved in many ways. A simple one is the case of oxidative–reductive photocatalytic reactions in liquid/solid systems using a solid

semiconductor (or insulator) catalyst. Typically, photons are absorbed by the solid photocatalyst particle in the fundamental absorption band (see Scheme 1) under photoexcitation of the solid by photons with $E = h\nu > E_g$, where E_g is the energy gap between the allowed electronic states in the valence band (VB) and conduction band (CB) of the semiconductors and insulators. Free charge carriers (photoelectrons and photoholes) are thereby photogenerated in the solid lattice and on the surface. They occupy allowed energy levels in the conduction and valence bands of the semiconductor, i.e. near the bottom of the CB band and near the top of the VB band, respectively. This occurs because of fast (typically less than ca. 10^{-10} s) relaxation of energy and momentum of the photogenerated carriers on interaction with the solid lattice. Ultimately, the excess energy of the carriers transforms into the energy of vibrational excitations (i.e. phonons) in the solids, subsequent to which the carriers/lattice phonons subsystem achieves thermal equilibrium. The quasi-continuous allowed electronic states (bands) in solids originate from discrete atomic (or ionic) energy levels owing to the distance between atoms (or ions) in solids. The energy gap (i.e. the absence of electronic levels in an ideal, defect-free solid) originates from the “remains” of the wide gaps of forbidden energy in the discrete spectra of free, spatially separated atoms and ions. Typically, only one gap exists in the energy spectrum of semiconducting and insulating solids as a result of the widening shift in crystal field, and overlapping of bands that correspond to high excited states of free atoms and free ions.

The transition of electrons from the occupied VB band to empty CB band levels occurs either through thermal processes or through absorption of light quanta (photoexcitation). The reverse electronic transitions (i.e. from the CB to the VB band) represent *recombination of electrons and holes*, i.e. recombination of charged carriers of the opposite signs. The theory of solids indicates that the properties of electrons remaining in the partially occupied VB band after transition of a small number of electrons to the CB band can be described by introducing the so-called concept of *holes* or



Scheme 1. Simplified Scheme 1 illustrating the photocatalyzed splitting of water on a semiconductor (or insulator) photocatalyst solid particle (see text).

quasi-particles with an effective positive charge equal to the absolute value of the electronic charge. Electrons and holes are delocalized (over the crystal lattice) electronic excitations. In the latter representation, there are neither electrons in the CB band, nor holes in the VB band in non-excited semiconductors and insulators at $T = 0$ K, and in the absence of actinic photons that might be absorbed by the solid, or in the absence of other external free energy sources. By contrast, electron–hole pairs are generated in photoexcited crystals. These pairs decay through either recombination or annihilation. Under continuous excitation, steady-state concentrations of carriers are established of a magnitude that depends on the rates of carrier generation and recombination.

The concentrations of electrons (n_e) and holes (n_h) in thermally excited semiconductors and insulators are determined by the mass action law (Eq. (5)):

$$n_e n_h = n_i = N_{CB} N_{VB} e^{-(E_g/kT)} \quad (5)$$

where N_{CB} and N_{VB} are the effective densities of states in the conduction and valence bands, respectively [40,41]. Typically, values of N_C and N_V are similar in magnitude and are in the range $(2\text{--}3) \times 10^{19} \text{ cm}^{-3}$ at ambient temperatures. The equivalent equations for electrons, n_e , and holes, n_h , are given by Eq. (6):

$$n_e = N_C e^{E_{CB}-F/kT} \quad n_h = N_V e^{E_{VB}-F/kT} \quad (6)$$

where F is the energy of the Fermi level (thermodynamic potential μ) of the carriers. For a perfect wide band-gap ($E_g \geq 3 \text{ eV}$) semiconductor and insulator, the Fermi level is located close to the middle of the forbidden energy gap with sufficiently high accuracy (to within a few 10ths of an eV). Thus, the concentrations of charge carriers in an ideal perfect wide band-gap solid are extremely low. In crystals with impurities (defects), the Fermi level shifts toward either the CB band (donor defects) or toward the VB band (acceptor defects), so that the concentration of electrons and holes, respectively, as given by Eq. (6) remains valid. At the same time, the concentrations of electrons and holes in wide band-gap solids determined by impurities inserted intentionally are typically less than those expected because of the effect of self-compensation of extrinsic conductivity [42]. Typically, even in highly imperfect wide band-gap solids, the Fermi level does not approach the CB or VB bands by energies less than 1–2 eV. The concentrations of thermal carriers are rather low at ambient temperatures, in accord with Eq. (6).

Under irradiation, the Fermi level of the catalyst splits into two quasi-Fermi levels: one for electrons (F_e) and the other for holes (F_h) provided that the relaxation times of momentum and energy of carriers are smaller than the lifetimes (determined by the recombination rate) of the charge carriers in the corresponding bands. Two Fermi quasi-levels correspond to two functions of the Fermi distribution for electrons and holes. Under irradiation, expression (5) becomes:

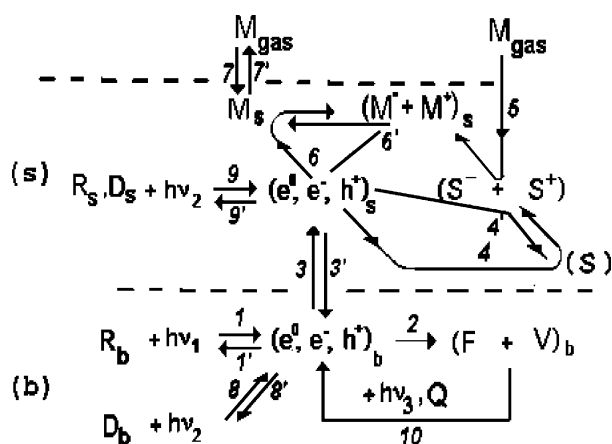
$$n_e n_h = n_i = N_C N_V e^{-(E_g - \Delta F)/kT} \quad (7)$$

where $\Delta F = F_e - F_h$. Note that in Eq. (6) for n_e and n_h , the symbol F is replaced by F_e and F_h , respectively. Note also that the higher the intensity of photoexcitation is, the greater is the Fermi level splitting, ΔF . Clearly, a catalyst subjected to irradiation behaves differently, with an apparent band gap given by $E_g - \Delta F$, which leads to changes in the concentration of free charge carriers. As a result, wide band-gap solids demonstrate increased activity in surface chemical processes and involve surface charge carriers.

In the simplest model of a photocatalytic reaction (Scheme 1), oxidation and reduction of molecules in a liquid/solid heterogeneous system occur as a result of electron transfer through the interfacial boundary. Accordingly, reduction occurs when the electron migrates from the solid to the electron acceptor molecule from the liquid phase, whereas oxidation occurs by the reverse electron transfer from the electron donor molecule from the liquid phase to the solid.

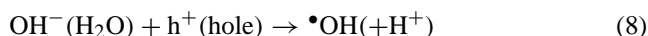
Scheme 1 illustrates both the space pattern (photocatalyst particle) and the energy pattern (band energy level diagram). In the energy diagram side, reduction is described by electron transition from the conduction band to the redox couple in the bulk solvent, whereas oxidation is depicted as the back-electron transition from the redox couple in the solvent phase to empty electron levels (i.e. occupied hole levels) of the valence band of the solid. Clearly, a pair of electron transitions to and from the solvent bulk (i.e. redox photoreaction) can be treated as recombination of photoelectrons and photoholes via an electrical circuit external to the solid catalyst. Thus, note the analogy between this kind of photocatalytic reaction with electrochemical or photoelectrochemical reactions. In the photocatalytic process, the photoexcited solid catalyst plays the role of both the electrical power supply and as the electrodes in the electrochemical cell. The electron transfer event is an exoergic process. Consequently, the reaction is possible when the redox potentials of the redox couple in the solvent are located at the proper positions relative to those of the bottom of the conduction band E_C and the top of the valence band E_V of the solid catalyst, or the positions of the so-called *flat-band potentials*. (For simplicity, band bending of the energy levels in the near-surface field, i.e. the so-called surface potential barrier, has been neglected in Scheme 1). At the same time, the populations of the CB and VB are determined by the rate of photon absorption under illumination (Eq. (7)).

In general, the system photocatalyst/reagents can be treated as an electronically excited system similar to the system of reagents in photochemistry. This is why endoergic photocatalytic reactions take place under the appropriate mutual positions of the E_C and E_V levels relative to the redox potentials of the reagents. It should be noted, however, that photocatalytic reactions in liquid/solid systems might be more complex. For example, water photolysis, which evolves molecular oxygen and hydrogen, represents a process that converts photon energy to chemical energy. Also note that photocatalyzed reactions may include



Scheme 2. Events taking place in the bulk (b) and at the surface (s) upon irradiation of the photocatalyst particle for a gas/solid heterogeneous system (see text for details of the various steps).

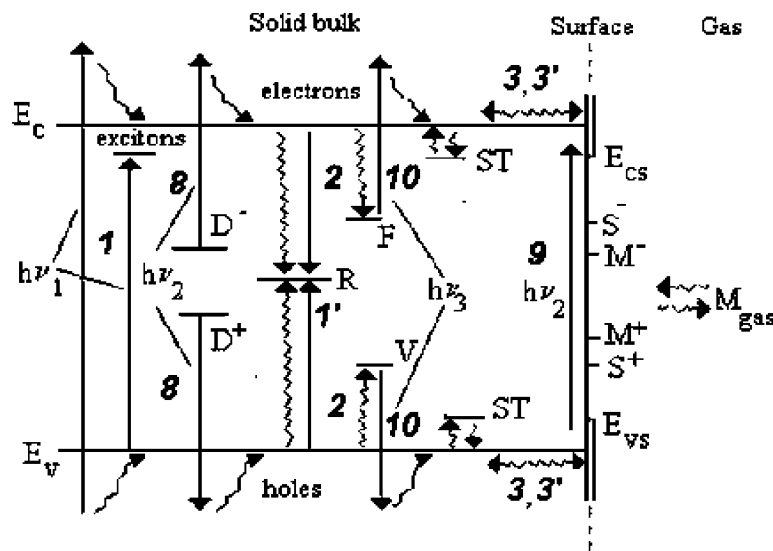
pre-adsorption of reagents as one of the initial steps. In this case, localization (trapping) of carriers on the adsorbed species plays the role of electron transfer noted above. They can also include such intermediate species as $\bullet\text{OH}$ radicals, which serve as oxidants and are formed through reaction 8 (for more details see [19]).



Gas/solid heterogeneous systems (the conducting phase that contains the reagents is absent) are far more complex than portrayed in the general Scheme 1 and as such the Scheme must be modified. The essential processes of photoexcitation and the subsequent processes that lead to photocatalytic reactions, photoadsorption and photodesorption for typical wide band-gap photocatalysts are illustrated in the somewhat more complex Schemes 2 and 3, respectively (energy diagrams only are shown).

The processes of photoexcitation of typical wide band-gap solids are rather complex. Henceforth, *photoexcitation* will signify any physical process that precedes the chemical interactions occurring at the photocatalyst surface. The majority of processes presented and described below are also valid for liquid/solid heterogeneous systems. In many cases, the appearance of photocarriers at the solid's surface is the essential outcome of photoexcitation (albeit not indispensable) in the photochemistry of the solid's surface. The carriers appear at the surface as a result of absorption of photons in the fundamental (*intrinsic*) absorption band (band-to-band transitions) of the solid (step 1, Schemes 2 and 3) and subsequent transport of the electron (e^-) and hole (h^+) carriers from the solid bulk to the surface (step 3). Band-to-band transitions in the regular crystal lattice (R_b) with generation of electron-hole pairs begin at the lowest photon energy $h\nu_1 = E_g$. For $h\nu_1 > E_g$, the excess energy of electrons and holes in the corresponding bands is converted to lattice phonon energy (or heat) due to relaxation (wavy arrows, Scheme 3) occurring at time scales less than $\sim 10^{-10}$ s. (As presented in Scheme 3, the energy of electrons in the CB increases in the positive (upward) direction of the energy axis (not shown), whereas the energy of holes in the VB increases in the opposite (downward) direction).

The lifetime of free carriers in the CB and the VB bands (typically greater than 10^{-10} s) is determined by the recombination of carriers (step 1'). In real (imperfect) wide band-gap solids, recombination of free carriers occurs through recombination centers (R, Scheme 3), i.e. via subsequent highly efficient trapping of electrons (holes) and holes (electrons) by the recombination centers R. These R centers typically have energy levels located near the middle of the forbidden energy gap. Recombination of carriers takes place by radiationless transformation of the electronic energy into lattice vibrations (phonons) (wavy arrows in



Scheme 3. Same events as Scheme 2 but portrayed differently.

Scheme 3), or via photon emission (recombination luminescence; *straight arrows*). Direct band-to-band recombination of carriers (not shown in Scheme 3) is insignificant in an imperfect wide band-gap solid [40]. The absorption of photons, which takes place even in perfect defect-free solids with creation of excitons, i.e. coupled electron–hole neutral (e^0) pairs (step 1, in Schemes 2 and 3), can also be attributed to fundamental absorption. Excitons can also interact with defects and reach the surface (steps 1 and 3 of Schemes 2 and 3) [43]. Depending on the nature of the solid, in particular, depending on its band-gap energy E_g , exciton absorption bands are located at energies from a few 100ths of an eV up to ca. 1 eV below the band-to-band absorption threshold. Typically, excitons dissociate into separate electron–hole pairs at ambient temperature due to interaction with lattice phonons.

Real solid particles contain imperfections (defects) of various kinds. Among these are the so-called point (zero-dimensional) defects and the regular surface itself (a two-dimensional defect). In turn, surface imperfections (surface point defects) are among the most important defects in heterogeneous photocatalysis and related phenomena [44]. Bulk *intrinsic* point defects include lattice vacancies, interstitial atoms and ions, and associated entities. *Extrinsic* defects also consist of interstitial atoms and ions, together with chemically different atoms and ions that substitute the native lattice atoms and ions. They are of a different chemical nature from the regular atoms and ions. The associated *extrinsic* and *intrinsic* defects are also found in imperfect solids. The theory of solids (see, e.g. [45,46]) indicates that any defect in the solid bulk (D_b in Scheme 1), i.e. any perturbation of the ideal crystal lattice, gives rise to a local electronic level. Defect levels located within the solid's forbidden energy gap are responsible for the so-called *extrinsic absorption* of solids. The corresponding absorption bands in the spectra of the solids occur in the low energy region ($h\nu_2$) with respect to the fundamental absorption bands ($h\nu_1$). The straight arrows (8 in Scheme 3) mark the photoelectrically active optical transitions between the bulk defects (D^- and D^+) and the CB and VB, respectively, yielding free carriers in the solid particle. In addition to the generation of carriers via the optical transitions mentioned above, trapping (or localization) of free carriers by defects (wavy arrows in steps 1' and 2 of Scheme 3) is essential for the photocatalytic behavior of the solid particle.

It is useful to classify the defects that trap free carriers in deep (R , F , V in Scheme 3) and shallow (SH) trap centers. They depend on the energy position ΔE of the corresponding center with a given trapped carrier with respect to E_C and E_V (Scheme 3). The difference ΔE determines the dominant decay pathway (the loss of trapped carrier) of a given center. For shallow traps, $\Delta E \approx kT$ at moderate temperatures, so that typically they decay via thermal excitation (thermal ionization), that is via interaction of shallow traps with lattice phonons. The latter process is negligible for deep (R , F , V) energy centers since $\Delta E \gg kT$. Those

that can subsequently and efficiently trap both electrons and holes serve as recombination centers (see above). By contrast, the so-called *color centers* of the F and V type denote efficiently trapped electrons (F centers) and holes (V centers), respectively. Accordingly, decay via recombination is relatively inefficient for color centers. A third decay pathway, namely photoionization, becomes a valid alternative for such deep energy centers (step 10 in Schemes 2 and 3). The color centers (pre-irradiation defect + trapped photocarrier), in contrast to recombination centers and shallow traps, accumulate in wide band-gap solids in amounts comparable to the number of corresponding pre-irradiation defects.

The long wavelength absorption bands of color centers typically occur in the visible red region relative to *extrinsic* absorption bands. The term *color centers* in wide band-gap solids originates from the color that is visually observed in bulk crystals or white powders following UV illumination. The condition of electroneutrality for free (e^- , h^+) and trapped (F , V) carriers (here we neglect the trapping of carriers by shallow traps and recombination centers) is given by

$$n_e + F = n_h + V \quad (9)$$

This equality is sufficiently accurate for $n_e \approx n_h$ such that

$$F = V \quad (10)$$

for both wide band-gap solids under continuous illumination and solids in the dark after illumination for a given period. However, because of sufficiently high rates of carrier recombination, the steady-state concentrations of photoelectrons (n_e) and photoholes (n_h) are smaller than for those carriers trapped in F and V centers, respectively.

We now describe further the above-mentioned properties of color centers for two reasons. First, the accumulation of color centers, i.e. the localized photocarriers separated in space, is also a form of storage of photon energy since the state of the solid particle with photoinduced color centers is a metastable energy state of the solid particle, with incomplete relaxation to the solid's ground state. Second, energy storage can also be achieved by surface chemical transformation of adsorbed molecules via secondary stimulation. The latter can occur either by thermal excitation (Q) or by absorption of low-energy photons ($h\nu_3$, step 10 in Schemes 2 and 3). Deep energy color centers can exist in pre-irradiated solids for an indefinite long time, especially at low temperatures, in the absence of secondary stimulation. Thus, processes of photon energy storage (for example, in the UV region, $h\nu_1$) and its achievement ($h\nu_3$, Q) can be delineated at extremely long times. It is relevant to note that shallow traps ($\Delta E \approx kT$ at ambient temperature) function as deep color centers at sufficiently low temperatures when $\Delta E \gg kT$. Note also that primary photoexcitation ($h\nu_1$) may include high-energy excitation by X-rays and γ -rays. In the latter case, relaxation processes of excess carrier energy will be more complex. However, photon energy will still be partly stored due to formation of color centers. Moreover, even in the case of generation of color centers by high-energy particle beams

(electrons, protons, neutrons and others), which introduces additional lattice defects by the so-called pathway of impact defect formation [47], storage of energy by the solid particle can still take place through a photostimulation step ($h\nu_3$).

The photoexcitation portion of the Scheme for the solid bulk sketched above (Schemes 2 and 3) can also be extended to photoexcitation of surface states [45,46] of the solid particle. In the general case, surface states correspond to the regular surface, i.e. regular crystal planes (R_s , in Scheme 2), and to various surface defects such as *intrinsic* (vacancies, atoms (ions), kinks, edges, corners) and *extrinsic* surface defects, including adsorbed species (D_s). The corresponding absorption bands are shifted to the red wavelength region and overlap with *extrinsic* bulk adsorption ($h\nu_2$ in Schemes 2 and 3). Thus, electrons, holes and excitons can appear at the surface as a result of photon absorption by the solid particle bulk followed by their diffusion and/or drift in the near-surface field (steps 1 and 3, 8 and 3, 10 and 3, in Scheme 2) and as a result of surface absorption (step 9).

The initial chemical stages of surface reactions with participation of free photocarriers may have different origins. The first is the trapping of carriers by surface pre-irradiated defects S (step 4 in Schemes 2 and 3), where S refers to photocatalytic (photoadsorption) centers [39]. Centers S can be surface defects of any kind noted above. In the state with trapped electrons (S^-) or holes (S^+), these centers are known as *active photocatalytic (photoadsorption) centers* or as the corresponding centers in their *active state*. The same active states can be formed in reactions between defects and excitons; thus,



These active centers interact with molecules in the gas (or liquid) phase (step 5 in Scheme 2) to yield the adsorbed species M_s^- or M_s^+ . If these intermediates (and M_{gas}) interact further, with or without the participation of surface electronic excitations to yield reaction products, their desorption into the gas phase and restoration of the initial state of the solid after each reaction cycle is then known as a *heterogeneous photocatalytic reaction* (Eq. (4)). The process that yields M_s^- or M_s^+ is referred to as *photoadsorption* of gas molecules, M_{gas} , as illustrated by the stoichiometric reactions:



Formation of the photoadsorbed species (or intermediates in photocatalytic reactions) M_s^- and M_s^+ can also occur through an interaction of mobile, weakly bound, pre-adsorbed molecules M_{ads} with the active photoadsorption (photocatalytic) centers S^- and S^+ (corresponding arrows are not shown in Scheme 2). Concomitantly, adsorbed species that may or may not be in adsorption equilibrium

(steps 7 and 7' in Scheme 2) with gaseous molecules can be treated as surface trap centers [48]. Thus, formation of M_s^- and M_s^+ can occur via step 6 (Scheme 2). In the latter case, regular surface sites can play the nominal role as a surface photocatalytic (photoadsorption) center S, whereas the free carriers on the surface play (in this particular case) the role of the active state of the photocatalytic center (S^- and S^+). Note that the chemical pathway of deactivation of active photocatalytic centers, including processes corresponding to Eqs. (12a) and (12b) and subsequent events, lead to the restoration of the photocatalyst. That is, restoration of the centers S competes with some physical pathways of deactivation of the active centers. In the case of photocatalytic reactions that involve trapping of free carriers by pre-adsorbed molecules (steps 6 and 7), or in the case of transfer of carriers to ions in the solvent medium (see above), the recombination of photocarriers takes place via recombination centers both in the solid particle bulk (step 1') and on the surface (step 9' in Scheme 2). When the surface center is some real point surface defect, the active state S^- or S^+ decays either by thermal ionization, or by recombination with a carrier of the opposite sign (step 4' in Scheme 2), or by photoionization of shallow or deep traps (see above).

The dominant pathway of decay of an active center determines its *lifetime*. If the active centers S^- and S^+ identify with a color center (F and V , respectively—see above), they accumulate on the surface during the primary photoexcitation and retain the ability to chemically react with gaseous or adsorbed molecules *in the dark* for a long time. This is known as the postsorption or post-catalytic effect—sometimes also referred to as the Coegelsbergs–Solonitzyn effect [49,50]. The memory effect of the Solonitzyn-type manifests itself as a photoreaction on a pre-irradiated surface. The delay time between the end of illumination and contact with molecules may exceed a few days at ambient temperature in laboratory experiments [51,52]. However, in view of the energy depth (>1 eV) of the active surface centers of a given color-center type, the *lifetime* of these centers in the active state may be indefinitely long even at ambient temperatures. (In the latter case, only tunneling recombination of the F and V centers can, in principle, restrict the lifetime of the active centers). Thus, the stages of photoexcitation of the solid particle and chemical interactions during photocatalysis in the interstellar media can be separated in time and, consequently, in space because of the migration of dust particles in atmospheric and interstellar dust clouds.

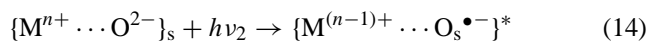
Other special features of heterogeneous photocatalytic reactions that may be of some relevance in gas/dust systems in the ISM and on primitive earth are now described below. Again we need to emphasize that photoinduced initiation of surface chemical reactions may occur via absorption of photons by the solid particle, and that the red spectral limit of chemical transformations may typically lie (i) far beyond the fundamental absorption edge of the solid and (ii) far beyond the red spectral limit of the corresponding photochemical reaction of free molecules. The red limits

of some heterogeneous photostimulated reactions (gas/solid systems) and band-gap energies E_g of solid photocatalysts are summarized in Table 2. All the wide band-gap solids show chemical activity far beyond their fundamental absorption threshold: $h\nu_2 < E_g$ (Scheme 2). Of course, these solids are also active when photoexcited in their fundamental adsorption band: $h\nu_1 \geq E_g$. Photoadsorption of simple molecules has been demonstrated for X-ray stimulated TiO_2 , ZnO , MgAl_2O_4 , and alkali earth fluorides (see references in the footnotes to Table 2). The activity of TiO_2 has been attributed to some bulk imperfections: D^+ for the photoadsorption of hydrogen and methane, and D^- for oxygen photoadsorption (Scheme 2). For ZnO , Volodin et al. [53] suggested primary photoexcitation of intrinsic surface states (E_{CS} and E_{VS}), as evidenced by ESR techniques for the alkali earth oxides. In the latter case, photoexcitation of surface intrinsic low-coordinated states ($\text{O}_{\text{LC}}^{2-}$) leads to direct formation of trapped holes (S^+ in our notation) and electrons at the surface (Eq. (13)).



The active state of the surface hole center (S^+) is represented as $\text{O}_s^{\bullet-}$ and is often referred to as a trapped hole. It has a *positive* charge with respect to the *neutral* oxygen site (O^{2-}) in the regular lattice of the metal oxides. Reaction 13 is an example of a surface photoreaction in which formation of the active catalytic center does not require carrier transport. The ultimate case of such a reaction is the reaction involving the photoexcitation of a surface vanadium center (Eq. (14)) [54]. Here the short-lived (ca. 10^{-2} to 10^{-4} s rel-

ative to the Coegel–Solinityn memory effect)



surface-active complex $\{\text{M}^{(n-1)+} \dots \text{O}_s^{\bullet-}\}^*$ displays activity in relation to methane photoadsorption. It should be noted that interaction of hydrogen-containing molecules with surface-active hole centers leads to dissociation of these molecules (see below). In fact, photoadsorption of this kind is the first step of a surface photochemical/photocatalytic reaction. Note that the more the localized centers (or defects) are excited in the primary stage of the reaction, the more similar are the photocatalytic and photochemical reactions.

The spectral limit of dissociation of adsorbed water on silica with adsorbed naphthalene (Np) is noted in Table 2 (last row). It is an example of a reaction with energy transfer from the upper T_1 state of adsorbed naphthalene to the triplet state of adsorbed water [55]. The former process originates from a two-step photoexcitation event: (a) via a spin-allowed electronic transition Np ($\text{S}_0 \rightarrow \text{S}_1$) followed by intersystem crossing Np ($\text{S}_1 \rightarrow \text{T}$), and then (b) via a triplet–triplet allowed transition Np ($\text{T} \rightarrow \text{T}_1$). The energy of the first optical transition determines the red limit of the reaction. It is worth pointing out that, typically, for naphthalene adsorbed on silica and for others, the energy of optical transitions of adsorbed molecules is somewhat significantly changed. In some cases, the photochemical behavior of adsorbed molecules can be treated simply as the photochemistry of the molecules perturbed by adsorption. However, such terminology as “absorption of light by adsorbed molecules” or “photolysis of adsorbed molecules”

Table 2
Band-gaps and red limits of photoadsorption and photolysis of small molecules on metal oxides

Solids	E_g (eV)	Photoadsorption, E_{red} (eV)			Photolysis, E_{red} (eV)	
		O_2	H_2	CH_4	H_2O	CO_2
TiO_2	3.2	2.2 ^a	~2.2 ^a	~2.2 ^a	~3.1 ^b	–
ZnO	3.2	1.7 ^a	–	2.1 ^a	–	–
MgO	8.7	4.0 ^c	2.7 ^c	3.0 ^c	4.9 ^b	–
$\gamma\text{-Al}_2\text{O}_3$	9.5	3.75 ^d	~4.0 ^d	~4.0 ^d	3.75 ^d	–
MgAl_2O_4	9.0	4.75 ^e	4.75, 3.1 ^{f,e}	4.75, 3.1 ^{f,e}	–	–
MgAl_2O_4 (Cr)	9.0	3.0 ^e	3.0 ^e	3.0 ^e	–	–
ZrO_2	5.4	3.1, 1.5 ^{e,c}	3.1, 2.2 ^{f,c}	3.1, 2.2 ^{f,c}	–	–
LiF	13.6	3.9 ^g	4.9 ^g	–	4.9 ^g	4.9 ^g
NaF	11.6	3.9 ^g	4.9 ^g	–	4.9 ^g	4.9 ^g
KBr	7.5	3.7, 1.6 ^{f,g}	–	–	4.9 ^g	4.9 ^g
SiO_2	>10	4.95 ^a	–	–	4.95 ^b	4.9 ^g
SiO_2 (V)	>10	–	3.7 ^h	–	–	–
SiO_2 (naphthalene)	>10	–	–	–	3.9 ⁱ	–

^a Basov et al. [51].

^b Basov et al. [64].

^c Emeline et al. [125].

^d Kotelnikov and Terenin [71].

^e Emeline et al. [97].

^f Red limit after UV pre-irradiation in vacuo.

^g Ryabchuk [63].

^h Shelimov and Kazansky [54].

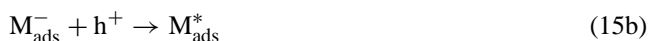
ⁱ Korotkov and Kholmogorov [55].

have meaning (in the sense mentioned above) only for weakly bound (physisorbed) small molecules, or for large molecules when the overall adsorption enthalpy is the sum of the adsorption enthalpies of a few relatively weak bonds. In the latter cases, the electronic structure of the M_{ads} species can be treated as the electronic structure of the molecule M perturbed by the environment (solid surface).

Direct photoexcitation of organic molecules adsorbed on dielectric solids (e.g. SiO_2 ($E_g > 10 \text{ eV}$) at energies far below the fundamental absorption threshold of the adsorbent is often referred to as “solid-assisted photocatalysis on *inactive* surfaces. In this case, participation of charge carriers in surface reactions can be neglected. Also, direct photoexcitation of adsorbed small molecules, including those relevant to abiogenesis and photocatalysis in the ISM (H_2 , O_2 , H_2O , CO_2 , CO , CH_4 , N_2 , NH_3 and others), can be neglected in the long wavelength region of photocatalyst activity. Such adsorbed species are best treated as specific surface defects in the solids [48]. Note that the electronic excited states of adsorbed species M_{ads}^* (to some extent, the latter are related to excited states of molecules) in this context may originate from direct absorption of photons (Eq. (15a)), or alternatively from trapping of the photocarrier



by the ionic form of the adsorbed molecule (Eqs. (15b) and (15c), or from subsequent trapping of



a photoelectron and photohole (or vice versa) for example—Eqs. (15d) and (15e).



Similar reactions with defects of the solid are often accompanied by recombination luminescence in the solids. For an adsorbed species, the decay of M_{ads}^* states often appears as photodesorption (see, e.g. [56–58]) in addition to deactivation and chemical transformation (reaction). The spectral limits noted by an asterisk in Table 2 are referred to as secondary photoexcitations ($h\nu_3$, Schemes 2 and 3) of color centers induced by the primary photoexcitation of the photocatalysts in the fundamental adsorption bands ($h\nu_1$). The red limits of the photoadsorption of oxygen (active centers with trapped electrons) and photoadsorptions of methane and hydrogen are different for a given metal-oxide system. The latter reflect the difference in the positions of the absorption bands of F and V color centers, which yield photoelectrons and photoholes, respectively (see Scheme 3).

4. Solid photocatalysts and photocatalyzed reactions

There exists a large body of experimental evidence to demonstrate heterogeneous photocatalysis (Eq. (4)) using both synthetic and natural solids as photocatalysts. Only a few solids, however, satisfy a number of conditions namely (i) the proper positioning of flat-band potentials relative to the redox potentials of couples in the solvent medium (see above), (ii) photocatalytic activity in the visible or near-UV region, (iii) resistance to chemical decomposition, and (iv) non-toxicity, among others. Taking into consideration the potential practical usage of photocatalysis with sunlight as the main free energy source and the above requirements, the majority of publications in heterogeneous photocatalysis has been devoted to studies of a few solid photocatalysts, but mostly on TiO_2 [20,21,57,59,60]. High turnover numbers (i.e. number of molecules produced per catalytic center during the reaction) are needed for practical photocatalysis. The latter is not a crucial point in the natural photochemistry of heterogeneous systems [27]. Even stoichiometric gas/solid reactions that yield partially gaseous or adsorbed products are of interest in natural processes. We sketch below a number of reactions and photocatalysts for which complete restoration of the photocatalyst during a large number of reaction cycles has not been confirmed. Such reactions are best referred to as *photoassisted* reactions.

The photochemical activity of solid surfaces has been established for many synthetic, simple and complex metal oxides (silicates, aluminosilicates, spinels,) ZnS , CdS and other such sulfides and chalcogenides [19,20,39,61,62], alkali halides and alkali earth fluorides [63].

The relative activities of different solids in the photolysis of adsorbed water were reported by Basov et al. [64] and are presented in Table 3. The powdered catalysts with pre-adsorbed water were photoexcited by a Hg lamp ($E_{h\nu} \leq 6.1 \text{ eV}$). The most active (first 15 systems in Table 3) photocatalysts are the wide band-gap solids ($E_g > 4.5 \text{ eV}$; see also Table 2). There exists an empirical correlation between the photoadsorption and the photocatalytic activities of the oxides and the energy of their band-gap E_g [65]. It is also noteworthy that several metal-oxide photocatalysts from Table 3 are made from elements of relatively high abundance in the Universe; some of these “metallic” elements are: O, Be, C, N, Si, Mg, Ar, Fe, Cl, Al, F, and others [66]. White and Zimmerman [67] have proposed an ISM dust grain core with an apparent formula $(\text{Mg}, \text{Fe}, \text{Si})_1(\text{Al}, \text{Ca}, \text{Ni})_{0.1}(\text{Cr}, \text{Mn})_{0.05}(\text{Ti}, \text{Ga}, \text{Cu}, \text{V})_{0.001}\text{O}_x$ for the silicate type. Clearly, the simple metal oxides from the dust grain formula are the likely photocatalysts (Table 2).

The last three decades have witnessed several workers [14,26,27,62] demonstrate the photocatalytic activity of a large number of natural substances (e.g. minerals, sands). Evidently, finding a solid photocatalyst in nature seems to pose no problem.

Photocatalytic reactions are classified in terms of oxidations, reductions, isomerizations, substitutions, condensa-

Table 3
Relative efficiencies of pre-adsorbed water photodecomposition with powdered solids [64]

Solid	Total reaction rate (a.u.)	Products evolving into the gas phase
BeO	100	H ₂ , O ₂
Be(OH) ₂	30	O ₂ , CO ^a , H ₂
γ-Al ₂ O ₃	30	H ₂ , O ₂
ZrO ₂	10	H ₂ , O ₂
La ₂ O ₃	9	H ₂ , O ₂
ThO ₂	8	H ₂ , O ₂
Na ₂ [AlF ₆]	7	H ₂ , O ₂
H ₃ BO ₄	6	O ₂ , CO ^a , H ₂
HfO ₂	6	H ₂ , O ₂
SrO	6	H ₂ , O ₂
SiO ₂	3	H ₂ , O ₂
Ho ₂ O	1	H ₂ , O ₂
Gd ₂ O ₃	<1	H ₂ , O ₂
Sc ₂ O ₃	<1	H ₂ , O ₂
MgO	<1	H ₂ , O ₂
TiO ₂	≪1	H ₂
ZnO	≪1	H ₂
GeO ₂	≪1	H ₂
Yb ₂ O ₃	≪1	H ₂
Dy ₂ O ₃	≪1	H ₂
Nb ₂ O ₅	≪1	H ₂
Zeolite NaX	≪1	H ₂
KBr	7	H ₂ , O ₂
KCl	0.4	H ₂
NaCl	0.5	H ₂
H ₂ O (snow) ^b	≈1	H ₂ , O ₂
Alumosilicate pure and Cr doped	≪1	H ₂

^a Thermal oxygen cleavage of sample surface was not available.

^b Irradiation at 200 K.

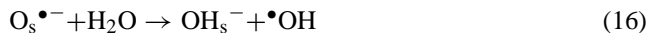
tions, and polymerizations [20]. Some of the various types of reactions involving mostly small molecules in gas/solid systems find a relationship to abiogenesis.

4.1. Decomposition of water and carbon dioxide

The photolysis of pre-adsorbed water likely occurs by two general mechanisms. The pioneering studies of De Boer [68], De Boer and Houben [69], and Terenin [70] treated the photodissociation of adsorbed molecules as occurring through direct photoexcitation (see above) into their red-shifted absorption bands. Basov et al. [64] also used this approach in their work. The observation that the red limits of photolysis were close to one another ($E_{\text{red}} = 4.9 \text{ eV}$) for different catalysts lent credence to the suggestion. That the grossly estimated red limit of the photolysis of “water snow” was nearly identical to that for adsorbed water and for the two-step photolysis of water photosensitized by adsorbed naphthalene [55] also supported the above notion. By contrast, Kotelnikov and Terenin [71] proposed an alternative reaction pathway in which the primary step involved photoexcitation of the solid photocatalyst.

Basov et al. [65] considered the formation of free $\bullet\text{OH}$ radicals and bound hydroxyl groups to arise from the

primary dissociative adsorption of water on photogenerated surface-hole centers as expressed by reaction 16. This assertion was based on their observation that photolysis



of adsorbed water in the presence of CO₂ and CO₂/CH₄ mixtures produced formaldehyde (H₂CO). The rate of hydrogen evolution into the gas phase is typically much greater than that of oxygen during water decomposition. Oxygen remains mostly chemisorbed on the surface, heating being required to obtain free photolytic oxygen in the gas phase. This is one reason why molecular oxygen is often not detected in low-activity catalysts (see Table 3). These workers [65] also noted that at elevated temperatures both oxygen and hydrogen evolve stoichiometrically with some increase in the reaction rate. The same occurs in the photolysis of CO₂ over alkali halides [63]. Dissociative photoadsorption of CO₂ evolves CO into the gas phase followed by CO photooxidation by adsorbed (photolytic) oxygen. Under continuous illumination the chemical equilibrium of this reaction appears to favor the products. The photolysis of CO₂ on alkali halides is an example of a photolytic surface reaction taking place through the primary excitation of the solid; pre-adsorption of the substrate is not a required condition.

4.2. Photoconversion of methane

The photoconversion and photooxidation of methane proceed by pathways not very different from those above. The reactions were first observed on a TiO₂ catalyst [72,73] and later extended to 12 other wide band-gap metal oxides [74]. This reaction is an example of a non-catalytic reaction, which likely plays a role in nature analogous to the photodecomposition of freons in modern earth's atmosphere [27,75]. The first step in the conversion of methane is dissociative adsorption on photogenerated hole centers (Eq. (17)). The recombination of methyl radicals leads



to formation of gaseous ethane (CH₃CH₃) and its subsequent dissociative re-adsorption on similar O_s^{•−} centers with formation of ethyl radicals, and so on. Formation of ethane, propane, ethylene and other hydrocarbons, together with partial (e.g. alcohols) and complete oxidation products of methane by lattice oxygen has been established. Ethylene is formed by H-atom extraction from the intermediate ethyl radical $\bullet\text{C}_2\text{H}_5$ by O_s^{•−} centers. The reaction is not photocatalytic at $T \leq 300 \text{ K}$. Extraction of hydrogen via the general reaction 18 yields stable OH_s[−] groups, which tend to

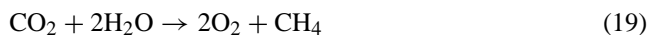


block the catalytic centers (surface hole traps). This latter process may be partly responsible for the non-catalytic character of methane conversion. Further details concerning the properties of hole centers on oxide surfaces and methane

conversion are given in the studies of Kazansky [76] and Krylov [77]. The surface density of photocatalytic centers in an inactive state *S* (Eqs. (11a) and (11b)) has been estimated to be around 10^{10} to 10^{12} cm⁻² for wide band-gap oxides [64]. This estimate reflects the amount of reaction products that can be obtained from a unit solid particle surface in non-catalytic photoreactions. Indeed the red limits of methane photoadsorption (Table 2) are actually the red limits of methane conversion and oxidation over the oxides.

4.3. Photofixation of CO₂

To our knowledge, the first report(s) on the photofixation of CO₂ (Eq. (19)) appeared for gas/solid systems some three decades ago on the (1 1 1) regular surface of SrTiO₃ [65,78]. The same process occurs on AgCl/zeolites [79].



UV illumination of an aqueous TiO₂ (nominally pure and doped) suspension in the presence of CO₂ produced formaldehyde, formic acid, methanol, and methane, among other products. Similar products were produced with SiC, CdS, GaP, ZnO, WO₃, and BaTiO₃ photocatalysts. The efficiencies of the reaction tend to be low because of the reverse oxidation reactions. Further details are given in several excellent reviews [20,21,57] and references therein.

4.4. Photofixation of molecular nitrogen

Both reductive and oxidative photofixation of N₂ have been reported. Schrauzer and Guth [80] detected NH₃ in the (H₂O + N₂)/TiO₂ system under UV illumination. Promotion of reactions 20 and 21 takes place over UV-illuminated pure and metal-doped (Fe, Cr, Mn, Co) TiO₂, WO₃, and ferric oxides (see e.g. [81] and references therein).

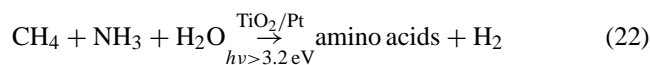


Adsorbed nitric oxides are formed from O₂/N₂ gas mixtures over an illuminated TiO₂ surface due to oxidative fixation of nitrogen [82]. However, the rates of N₂ fixation are extremely low; accordingly, some of the published results on N₂ fixation must be viewed with some uncertainties [21]. The reverse reaction, namely the photodecomposition of adsorbed ammonia is also known. As long ago as 1941, Kasparov and Terenin [83] first noted that photolysis of NH₃ pre-adsorbed on alumina evolves molecular hydrogen into the gas phase.

4.5. Addition of amino acids and peptides

A number of amino acids such as glycine, alanine, glutamine, aspartic acid, and serine have been photosynthesized

from methane and ammonia over aqueous platinized TiO₂ suspensions [84]. The overall reaction is



Platinum accelerates formation of H₂ in the reaction. Methanol, ethanol and methylamine are produced as attendant products. Other experimental studies have used other precursors to achieve the abiogenesis of amino acids [85–87] and a variety of polyaromatic hydrocarbons (PAHs) and other conjugated molecules [88].

The synthesis of peptides from amino acids over TiO₂ has been achieved [89], as was oligomerization of ribonucleotides on a mineral surface (montmorillonite) achieved by reaction of 5'-phosphorimidazolidine of adenosine, (ImpA) [90]. Similar reactions can be promoted by UV and X-ray irradiation of adenosine-5'-monophosphate (5'-AMP) molecules adsorbed on mineral surfaces (mostly clays) [91–93]. Thus, even a selected number of reactions mentioned above as examples shows that a priori one may expect to find heterogeneous photosynthetic reactions in nature.

5. Additional features of heterogeneous photoreactions

5.1. Dependence of kinetics on light intensity and pressure

The dependence of rates of heterogeneous photoreactions on pressure and light intensity is given by the Langmuir–Hinshelwood (LH) kinetic expression (Eq. (23)):

$$r(I, p) = \frac{kKp}{1 + Kp} \quad (23)$$

where *k* and *K* are constants for a given light intensity. In earlier studies (see for example [19] and references therein) the Langmuir constant *K* was referred to as the Langmuir adsorption/desorption constant $K = k_{\text{ads}}/k_{\text{des}}$. The dependence of the rate on light intensity *r(I)* is determined by the rate constant *k* only by the dominant pathway of carrier recombination. Thus, adsorbed molecules act as traps of photocarriers in the mechanism (see above). Other pathways involving the participation of surface centers and intermediates have also been proposed for liquid/solid systems [94]. Details of the LH kinetics were re-investigated by Emeline et al. [95,96]. The first-order rate constant (*k*_{des} in the original mechanism) was attributed to the apparent decay constant of the active state of the catalytic center (*S*⁻ or *S*⁺, Schemes 1 and 3). For the cases of photoionization or recombination decay of active centers (process 4', Scheme 2), Eq. (23) becomes:

$$r(I, p) = \frac{alp}{bI + cp} \quad (24)$$

where *a*, *b*, and *c* are constants. It is evident that at extremely low gas pressures the reaction rate does not depend

on light intensity (photon flux). This is the case when the reaction proceeds via long-lived active centers (memory effect, see above). Whatever the mechanisms considered, the heterogeneous reactions can proceed at very low light intensities and gas pressures provided that the extent of pre-adsorption of molecules is significant (see also [59]). These conditions are typical of cosmic dust environments (see below).

5.2. Temperature dependence

Temperature dependencies of heterogeneous reaction rates can be considered a priori as rather complex because they typically include several stages. Simply stated, the photoexcitation of solids starting with the adsorption of light quanta up to the generation of active centers in the ideal case can be considered as a non-activated process. However, the “hopping” diffusion and/or drift of carriers (electron and hole transport during the photoreaction) in amorphous solid particles may be activated processes. A few studies (see, e.g. [97–100]) have been devoted at examining temperature dependencies of photoadsorption dynamics. At elevated temperatures the photoadsorption rates typically decrease as the temperature increases at temperatures greater than 300–400 K owing to the thermal destruction of active centers and desorption of adsorbed species. By contrast, the rates increase with decrease in temperature at temperatures below 300 K in some region down to 150–200 K for ZnO and TiO₂. The data concerning the activation energies (E_a) of adsorption stages ($S^+(S^-) + M \rightarrow M_{ads}$) are somewhat uncertain. For example, the $E_a = 4.2 \pm 0.8$ kJ/mole at temperatures around 150 K was established for CO adsorption on photogenerated hole $O_s^{\bullet-}$ centers in ZnO [99,100]. At the same time, the E_a for dissociative adsorption of hydrogen on $O_s^{\bullet-}$ centers on the surface of alumina seems to be smaller. The intensity of the luminescence glow accompanying the adsorption does not decrease up to 77 K [101].

The rates of migration of adsorbed CO on a TiO₂ particle surface are sufficient to allow CO to be photooxidized at $T \approx 100$ K [57]. The photogenerated $\bullet CH_3$ radicals (see below) on the ZnO surface remain mobile even at 90 K [102]. Thus, the first photoinduced stages of photocatalytic reactions can occur in a wide range of temperatures. For example, photolysis of adsorbed water on BeO occurs in the range of 77–800 K, and the efficiencies at the two extreme temperatures of the range are twofold smaller than the maximal observed efficiency [65]. Consequently, we can infer possible occurrences of various heterogeneous reactions leading to the synthesis of complex molecules in Interstellar Space. The *a priori* we also deduce that the higher the number of stages that involve the participation of chemical intermediates in the photoreaction mechanism, the higher will be the probability of finding an activated process. The same problems will be encountered as for any surface reaction that is induced by other types of energy sources.

5.3. Process efficiencies

The problems of comparing efficiencies of heterogeneous photoreactions have been discussed in some detail in several recent reports (see, e.g. [65,103]). To estimate efficiencies of natural photocatalysts, one needs to know the spectral dependence of the photochemical quantum yield for a given reaction.

The quantum yield of heterogeneous photoreactions stimulated by monochromatic light is given by the relationship 25:

$$\Phi = \frac{dN_{mol}/dt}{dN_{ph}/dt} \quad (25)$$

where dN_{mol}/dt is the number of molecules produced (or consumed) per unit time and dN_{ph}/dt is the number of photons absorbed by the system or, typically, by the solid catalyst per unit time. For exhaustive processes (photoadsorption, photodesorption, non-catalytic reactions) the maximal initial quasi-stationary rate of reaction is taken to calculate the quantum yield so as to characterize the most active state of the photocatalysts.

Generally, the quantum yield Φ depends on the reagent concentrations (pressure of gas) and light intensity, as well as on other parameters of the solid catalyst particle (see, [58]). To compare efficiencies of different photocatalysts, the kinetic region to be considered is one in which the reaction rates are independent of concentration; that is, for $Kp \gg 1$ in Eq. (23). In the latter case, Φ is the quantum yield of formation of active catalytic centers. Emeline et al. [104] have used a theoretical approach to describe the $\Phi(h\nu)$ dependence. These researchers modeled a solid catalyst particle as an infinite plate with thickness d illuminated by a parallel photon flux I . The surface reaction rate of formation of active centers (i.e. the numerator in Eq. (25)) was taken as $dN_{mol}/dt = k_{tr} S n_s$, where k_{tr} is the rate constant of carrier trapping by surface centers with concentration S , and n_s is the steady-state concentration of photocarriers at the surface. The surface concentration of the charge carriers n_s is given by the solution to the continuity equation:

$$D \frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x)}{\tau} + g(x) = 0 \quad (26)$$

where $n(x)$ is the concentration of photoelectrons at point x in the crystallite particle bulk, D the diffusion coefficient of electrons, and τ is the lifetime of the free photoelectrons with respect to all the recombination channels in the solid bulk. The first term in Eq. (26) describes electron diffusion, whereas the second term describes the pseudo-first-order decay of free carriers. The non-uniform function of the generation of photocarriers, $g(x) = \beta \alpha I \exp(-\alpha x)$ corresponds to the Lambert–Beer absorption law, where β is the probability of carrier generation on absorption of photons and α is the Lambert–Burger absorption coefficient. The rate of surface recombination of carriers is included in the boundary conditions that describe the decay of carriers on

the surface owing to recombination and trapping (for further details, see [104]). The general expression for Φ was obtained from a complex expression; Eq. (27) expresses the several parameters involved.

$$\Phi(h\nu) = f\{\beta, k_{tr}, S, D, d, L, s, \tau, \alpha(h\nu)\} \quad (27)$$

where the diffusion length of carriers L is given by $(D\tau)^{1/2}$. Clearly, the detailed expression for the $\Phi(E)$ function is not trivial [104]. Nonetheless, it is possible to simplify the relationship. For example, when $1/\alpha \ll d$, the quantum yield Φ becomes independent of photon energy. This case is valid for very small particles. Typically, the absorption coefficients α lie around 10^5 to 10^6 cm^{-1} in the fundamental absorption band of solids. In addition, if only thermally relaxed carriers occupying the states near the top of the valence band and the bottom of the conduction band (Scheme 3) participate in the reaction, then the spectral independence of β assures the absence of any spectral dependence of Φ . In the general case, $\Phi(h\nu)$ should be obtained from laboratory studies. Experimental spectral dependencies of $\Phi(h\nu)$ for the photolysis of adsorbed water on alumina and for the photoadsorption of oxygen, hydrogen and methane over rutile TiO_2 particles are presented in Figs. 2 and 3, respectively. Clearly, the Φ values are separately dependent and β is not spectrally independent; that is, non-thermally relaxed charge carriers are involved in the heterogeneous photoreaction.

In practice, the quantum yield Φ does not depend on light intensity in the region where the reaction rate scales linearly with light intensity (or photon flux). In such case, the total surface reaction rate r of a photoreaction in a heterogeneous system under illumination by non-monochromatic

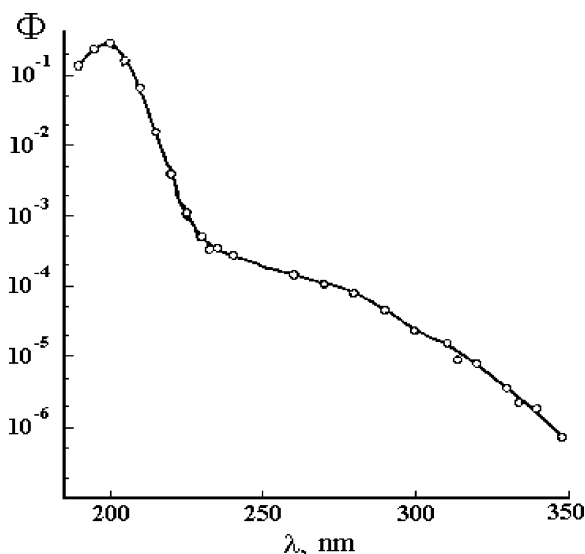


Fig. 2. Spectral dependence of the quantum yield of the photolysis of water on Al_2O_3 particles. The surface of the adsorbent had previously been hydrated by heating the alumina particles in water vapor at 250°C for 6 h. (Note the logarithmic plot of Φ).

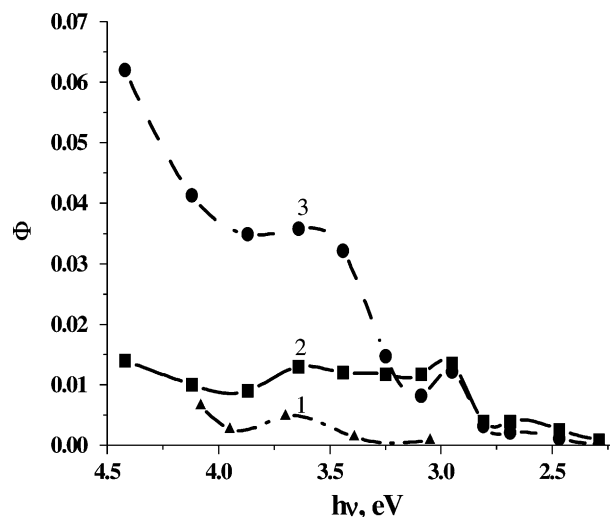


Fig. 3. Spectral dependencies of quantum yields of photoadsorption of oxygen (1) at $T = 100 \text{ K}$, hydrogen (2), and methane (3) on powdered TiO_2 (rutile).

light within a given spectral interval of photon energy ($h\nu_1$, $h\nu_2$) is given by (Eq. (28)),

$$r = \int_{h\nu_1}^{h\nu_2} \Phi(h\nu) A(h\nu) \rho(h\nu) d h\nu \quad (28)$$

where $A(h\nu)$ is the spectral dependence of the dimensionless absorption coefficient of a catalyst (or heterogeneous system), $\rho(h\nu)$ is the spectral density of the incident photon flow expressed by the number of photons per centimeter square per unit time per unit energy interval.

Strictly speaking, the quantum yield and the reaction rate refer to a single photocatalyst particle. The catalyst particle plays the same role of a chemical entity (molecule, atom) in photochemistry and in homogeneous molecular photocatalysis. Contrary to atoms and molecules, however, photocatalyst particles are not identical. They each differ in size, nature of surface, surface defects, and bulk defects among others. In practice then, Φ and other quantities are obtained in laboratory experiments in heterogeneous photocatalysis as an integrated parameter over the ensemble of particles, i.e. over a dispersed sample of the catalyst in laboratory studies, or as the dust cloud in the ISM. Irradiation conditions are usually non-uniform in a photoreactor (for photoadsorption and photocatalysis) containing a dispersed sample (system) because of light absorption, light scattering, reactor geometry, and others [65]. However, the condition of uniform irradiation is always valid for a given point in a small differential volume of the sample. The quantum yield can be expressed as $\Phi = q/E$, where q is the number of molecules produced on a unit of a uniformly irradiated surface per second ($\text{mol cm}^{-2} \text{ s}^{-1}$), and E is the number of photons absorbed by this unit surface ($\text{photon cm}^{-2} \text{ s}^{-1}$).

The apparent quantum yield Φ^* integrated over the surface S of the sample, that is on a non-uniformly irradiated surface,

is given by Eq. (29):

$$\Phi^* = \frac{\int_s q \, dS}{\int_s E \, dS} = \frac{\int_s \Phi E \, dS}{\int_s E \, dS} \quad (29)$$

If Φ is independent of E or of the incident photon flux (i.e. $E \sim I$), or in other words if the rate of the photoreaction is directly proportional to the incident photon flux, then

$$\Phi^* = \frac{\Phi \int_s E \, dS}{\int_s E \, dS} = \Phi \quad (30)$$

i.e. the apparent quantum yield measured for a non-uniformly irradiated surface is equal to the quantum yield for a uniformly irradiated surface. In the latter case there is no need to know the spatial distribution of the light intensity $I(x,y,z)$ in the dispersed non-homogeneous sample bulk (dust cloud). The latter favors the laboratory modeling of natural interstellar photocatalysis.

5.4. Spectral selectivity

The spectral selectivity of photocatalysts, or the dependence of the relative chemical yields of various reaction products for a given reactant on the energy of the actinic photons for a given photocatalyst, favors the synthesis of various organic substances in dust clouds. This effect was first reported for the oxidation and conversion of methane over the same surface of TiO_2 particles stimulated by photons in a wide spectral range, from the visible region up to X-rays [73]. The relative yield of conversion products (ethane, ethylene and others) was much greater than the yields of oxidation products (water, carbon dioxide and others) under illumination of TiO_2 by visible light and X-rays. By contrast, the relative yields of oxidative products prevailed on photoexcitation of TiO_2 in the fundamental absorption band (UV region). Similar selectivity was established for alkali halide photocatalysts with respect to the photooxidation of CO and for the reverse reaction of CO_2 photolysis [63].

The approach to a quantitative description of spectral selectivity in relation to oxidative and reductive reactions has been presented elsewhere [105]. Briefly stated, the rate of the oxidation reaction depends on the surface concentration of photoholes $[\text{h}_s^+]$, whereas the rate of the reduction reaction depends on the surface concentration of photoelectrons $[\text{e}_s^-]$. These two concentrations are different on the particle surface, and their ratio depends on $\alpha(h\nu)$ and on other parameters (see Eq. (27)). In fact, the oxidation of methane over irradiated titanium dioxide, which yields water and carbon dioxide, prevails in the UV part of the fundamental absorption band where $1/\alpha < d$. In contrast, the rate of methane conversion is higher on excitation of TiO_2 in the X-ray region of the fundamental absorption band of TiO_2 , and in the *extrinsic* absorption bands (visible) where $1/\alpha \ll d$. Note that the spectral selectivity is indirectly determined by the energy of the actinic photons, i.e. by the spectral dependence of the absorption coefficient α of the photocatalyst. The spectral selectivity and the quantum yield

are also properties of a single catalyst particle. However, the interesting feature appears in the ensemble of particles because of spectral selectivity. In the dispersed dust cloud the depth of photon penetration, which would correspond to the weak (small α) limit of absorption of dust particles, is much greater than that for the strong absorption limit (i.e. for large α). Consequently, if the appropriate type of spectral selectivity of TiO_2 takes place, in addition to ordinary UV screening effects in clouds, the synthesis (polymerization) of organic substrates will take place in the inner sites of the dust cloud illuminated by distant light sources (stars). For example, the heterogeneous system involving dust particles in the primitive earth's oxygen-free atmosphere might have served as a "self-protecting" system in relation to the synthesis of organics in a manner similar to the "life-protecting" ozone layer that occurs in the modern earth's atmosphere.

6. Relevance of heterogeneous photochemical reactions to interstellar abiogenesis—issues and perspectives

Taking into consideration the existence of solid photocatalysts in Interstellar Space [106–111], the promotion of biologically significant reactions on photocatalyst surfaces irradiated in a wide range of photon energies, photon fluxes, and at several temperatures and gas pressures, together with some of the special features of heterogeneous systems favorable to abiogenesis discussed above, the qualitative forecast of the significant role of heterogeneous photochemistry in interstellar abiogenesis appears attractive and encouraging. However, quantitative estimates based on realistic models are needed to compare the efficiencies of heterogeneous photochemistry in nature with those of other pathways of abiogenesis. Tentative estimates have been reported by Basov et al. [112]. It was assumed that about 1% of the earth's surface is coated by a hypothetical solid photocatalyst layer 1–2 mm thick with a dimensionless reflectance $R = 0.9$. The latter is typical of wide band-gap solids in the *extrinsic* absorption bands. In this case, the dispersed layer consisting of micron-size particles can be considered to be opaque; absorbance $A = 0.1$ (Eq. (28)). Note that for the fundamental absorption band, $A \approx 1$; that is it is about 10-fold higher (for powders). Grosso modo, we can also consider that an equal amount of catalyst is dispersed in the atmosphere as dust. The photon flow $\rho(h\nu)$ (Eq. (4)) was taken as that of the modern earth's troposphere. Under these assumptions, the rate of water photolysis ($\Phi(h\nu) = 0.001 = \text{const}$; red spectral limit is the same as for alumina, see Fig. 2) was estimated to be $\sim 10^{10}$ kg per year, and the rate of methane conversion to be around $\sim 10^8$ kg per year ($\Phi(h\nu) = 0.01$; red limit same as for titania; see Fig. 3).

From the above estimates, approximately 10^7 – 10^8 years are needed to produce the amount of oxygen by water photolysis that equals the quantity of oxygen in the atmosphere, or to transform carbon from C1 to C2 (methane to ethane) in amounts equal to that for carbon in the modern biosphere.

The reverse reactions were not included and the hypothetical “dust” was considered as the photocatalyst. Consequently, these estimates must be regarded as tentative at this stage. Nonetheless, the estimated rates obtained compare well in order of magnitude with those of the formation of formaldehyde by direct photolysis of H_2O and CO_2 in the UV clear troposphere with extraction of formaldehyde H_2CO in oceans for a well-known purely photochemical model [113]. The time period for the complete photochemical polymerization of methane in the primitive earth’s atmosphere with formation of a thin polymer film on the land surface and oceans has been estimated to be around 10^8 years [114,115].

More realistic models have suggested much faster rates of heterogeneous photoreactions in modern earth’s atmosphere. The results are in satisfactory accord with the monitored data. For example, Pozdnyakov et al. [25] have proposed that the minimum concentration of $\bullet\text{CCl}_3$ found above the Sahara desert might be explained by the heterogeneous photocatalytic destruction of CCl_4 on mineral particles that migrate from the earth’s surface to the upper atmosphere. Others reached the same conclusions [116,117]. The latter workers estimated the concentration of CO_2 produced in heterogeneous photocatalytic oxidations of organic substrates adsorbed on atmospheric silicates (sands) above California to be ca. 1.8×10^{12} kg CO_2 per year, equal to ca. 30% of the carbon dioxide produced by industrial anthropogenic emissions. The effective decay of freons via heterogeneous photoreactions on aerosols over Siberia has also been demonstrated [27,75].

From the above discussion and on the basis of a gross comparison of purely photochemical and heterogeneous photochemical pathways of abiogenic syntheses and other photostimulated reactions on earth, we conclude that studies on the possible contributions of heterogeneous photochemistry/photocatalysis to abiogenesis occurring under primitive earth’s conditions encourage further explorations.

Studies and modeling of heterogeneous photoreactions in distant interstellar ISM sites, such as for example in dark molecular clouds, seem less encouraging but nonetheless intriguing. Several issues must be solved to get more realistic estimates of the rates of heterogeneous photochemical reactions (including zero-order reaction rates, i.e. the failure of the hypothesis) at various sites in interstellar space. The first problem is to find a given reaction in a laboratory environment using solid particles that model *real* dust particles. The simplest case is the modeling of the photochemical behavior of the system *gas/“mantleless” particle* (dust grain). It could work on dust zones at temperatures $T > 100$ K. Even in this case, however, the underlying problem is the absence of enough information and data about the chemical consistency, size, structure and other properties of dust grains.

As noted above, the solid particle plays the role of a chemical entity in chemistry and photochemistry so that in contrast to molecules it may not be possible in practice to reproduce interstellar dust particles in the laboratory. Accordingly, some probabilistic model of a “typical dust grain

particle” (or a few models) based on a large body of experimental data is needed. The solid mineral particles coated by an icy mantle are very interesting but very poorly investigated and understood relative to heterogeneous photocatalyst particles. A similar system (atmospheric aerosols coated by water ice) was treated briefly recently [27]. The system consisted of three phases (for sufficiently large particles). The two-component solid photocatalysts (i.e. semiconductor heterostructures) such as TiO_2/CdS and $\text{TiO}_2/\text{SnO}_2$ [118–120] can serve as analogs of dust particles at temperatures below 80–100 K in ISM space. In this way, carbonaceous ice-coated particles may to some extent behave similarly to metal–dielectric micro/nano heterostructures. On the other hand, the icy mantle itself is a very specific solid component of dust particles. In short, contrary to ordinary binary solid catalysts, not only electronic processes occur in the icy mantle but also chemical reactions. With the exception of pure nitrogen, the icy mantle itself is also photochemically active [18,64]. It should be noted that ultrasmall dust particles could also behave as quantized nanoparticles [121] as a result of the quantum confinement effect. Tunneling of photocarriers is a valid electron transport method for the photocatalytic behavior of such Q-sized particles [122–124].

A strategy of modeling the dust particle environment in the laboratory (extremely low temperatures and very low gas pressures) needs to be developed in the case of heterogeneous photoreactions. For example, the interdependence of reaction rates on gas pressure (or concentration) and light intensity I (Eq. (23) or Eq. (24)) can lead to difficulties in modeling the “cosmic time period” in short-time scale laboratory experiments since the number of molecules N that react on cosmic dust particles is coupled to both light intensity I and time t . That is, N will not scale linearly with It under normal laboratory conditions because of the small number of N molecules on the particles. However, the photochemically active ice on the grain–mantle boundary is to some extent similar to a cold but very dense gas or non-polar liquid. It is possible to increase the surface density of molecules on dust particles at very low temperatures in the experimental modeling of interstellar chemistry such that $N \propto f(It)$ and Eq. (24) becomes relevant again. Under these conditions, the “cosmic” time component can be shortened considerably by increasing the light intensity for reasonably high N .

Some special events of heterogeneous photochemical processes such as the memory effect and the possibility of releasing the stored energy and carriers via secondary excitation in the long wavelength regions (see above) may also occur at low temperatures. An example is the UV-induced secondary infrared activity of a photocatalyst particle, because at low temperatures the very shallow carrier traps may behave as deep energy centers do at elevated temperatures.

In conclusion, we deduce that there does exist a role of heterogeneous photochemical/photocatalytic reactions in natural abiogenesis in the interstellar medium and on the

primitive earth. The details of what this role is remain to be clarified.

Acknowledgements

The work carried out in Montreal is supported by the Natural Sciences and Engineering Research Council of Canada (to N.S.).

References

- [1] S.L. Miller, H.C. Urey, J. Oro, Origin of organic compounds on the primitive earth and meteorites, *J. Mol. Evol.* 9 (1976) 59–72.
- [2] S.L. Miller, L.E. Orgel, *The Origin of Life on the Earth*, Prentice-Hall, Englewood Cliffs, NJ, 1972.
- [3] S.W. Fox, K. Dose, *Molecular Evolution and the Origin of Life*, W.H. Freeman, San Francisco, 1972.
- [4] P. Ehrenfreund, S.B. Charnley, Organic molecules in the interstellar medium, comets, and meteorites: a voyage from dark clouds to the early earth, *Ann. Rev. Astron. Astrophys.* 38 (2000) 1–51.
- [5] National Radio Astronomy Observatory, “The 123 Reported Interstellar and Circumstellar Molecules, Updated 11 April 2002 by HAW”, see their website <http://www.cv.nrao.edu/~awooten/allmols.html>.
- [6] S.B. Charnley, P. Ehrenfreund, Y.J. Kuan, Spectroscopic diagnostic of organic chemistry in the protostellar environment, *Spectrochim. Acta, Part A* 57 (2001a) 685–704.
- [7] S.B. Charnley, S.D. Rodgers, Y.-J. Kuan, H.-C. Huang, Biomolecules in the Interstellar Medium and in Comets, Preprint Archives Astrophysics, 2001b, pp. 1–13, arXiv:astro-ph/0104416—see also website <http://xxx.lanl.gov/pdf/astro-ph0104416>.
- [8] I. Prigogine, in: Ch.C. Thomas (Ed.), *An Introduction to the Thermodynamics of Irreversible Processes*, Springfield, 1955.
- [9] A.I. Oparin, *The Origin of Life on Earth*, Academic Press, New York, 1957.
- [10] T.E. Pavlovskaya, Abiogenic synthesis of biologically important compounds, in: A.I. Oparin (Ed.), *Problems of Origin and Essence of Life*, Nauka, Moscow, 1973, pp. 38–72 (in Russian).
- [11] A.R. Hochstim, The role of shock waves in the formation of organic compounds in the primeval atmosphere, in: R. Buvet, C. Ponnampuruma (Eds.), *Proceedings of the International Conference on the Origin of Life, Chemical Evolution and the Origin of Life*, North-Holland Publishing Company, Amsterdam, 1971, pp. 96–106.
- [12] C.I. Simionescu, F. Denes, Originea vinetti. (Origin of Life), Romanian Academy of Sciences, Bucharest, 1983 (in Romanian).
- [13] H.D. Holland, *The Chemical Evolution of Atmosphere and Oceans*, Princeton University Press, Princeton, NJ, 1984.
- [14] M.A.A. Schoonen, Y. Xua, D.R. Strongin, The introduction in geocatalysis, *J. Geochem. Explor.* 62 (1998) 201–215.
- [15] M. Spaans, P. Ehrenfreund, The interstellar medium: a general introduction”, in: P. Ehrenfreund, et al. (Eds.), *Laboratory of Astrophysics and Space research*, Kluwer Academic Publisher, Dordrecht, 1999, pp. 1–36.
- [16] A. Li, J.M. Greenberg, A unified model of interstellar dust, *Astron. Astrophys.* 323 (1997) 566–584.
- [17] A.G.G.M. Tielens, W. Hagen, Model calculations of the molecular compositions of interstellar grain mantles, *Astron. Astrophys.* 114 (1982) 245–260.
- [18] P.A. Gerakines, W.A. Schutte, P. Ehrenfreund, Ultraviolet processing of interstellar ice analogs. Part I. Pure ices, *Astron. Astrophys.* 312 (1996) 289–305.
- [19] N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis—Fundamentals and Applications*, Wiley, New York, 1989.
- [20] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, *Chem. Rev.* 93 (1993) 341.
- [21] A. Mills, S. Le Hunte, An overview of semiconductor photocatalysis, *J. Photochem. Photobiol. A: Chem.* 108 (1997) 1–35.
- [22] A.N. Terenin, in: A.I. Oparin (Ed.), *The Origin of Life on Earth*, Academy of Sciences, USSR, Moscow, 1959, pp. 144–146 (in Russian).
- [23] S.F.-S. Chun, K.D. Pang, J.A. Cutts, J.M. Ajello, Photocatalytic oxidation of organic compounds on Mars, *Nature* 274 (1978) 875–876.
- [24] J.S. Hubbard, J.P. Hardy, N.H. Horowitz, Photocatalytic production of organic compounds from CO and H₂O in simulated Martian atmosphere, *Proc. Natl. Acad. Sci. USA* 68 (1971) 574–578.
- [25] D.V. Pozdnyakov, V.N. Filimonov, K.Ya. Kondratjev, Possible heterogeneous mechanism of discharges of freons and carbon tetrachloride in the atmosphere, *Dokl. Akad. Nauk SSSR (Reports of the Academy of Science, USSR)* 252 (1980) 1097–1100.
- [26] V. Isidorov, E. Klokova, V. Povarov, S. Kolotova, Photocatalysis on atmospheric aerosols: experimental studies and modeling, *Catal. Today* 39 (1997) 233–242.
- [27] V.N. Parmon, V.S. Zakharenko, Photocatalysis and photosorption in the earth atmosphere, *CATTECH* 5 (2001) 96–115.
- [28] S.V. Surdin, *The Birth of Stars*, UPSS Publishing House, Moscow, 2001 (in Russian).
- [29] F.H. Shu, F.C. Adams, S. Lisano, Star formation in molecular clouds, *Ann. Rev. Astron. Astrophys.* 25 (1987) 23–81.
- [30] S.B. Charnley, in: C.B. Cosmovici, S. Bowyer, D. Wertheimer (Eds.), *Astronomical and Biochemical Origins and Search for Life in the Universe*, Editrice Compositori, Bologna, Italy, 1997, pp. 89–96.
- [31] T.I. Hasegawa, E. Herbst, New gas–grain chemical model of quiescent dense interstellar clouds: the effect of H₂ tunneling reactions and cosmic rays induced desorption, *MNRAS* 261 (1993) 83–102.
- [32] T. Kasamatsu, T. Kaneko, T. Saito, K. Kobayashi, Formation of organic compounds in simulated interstellar media with high-energy particles, *Bull. Chem. Soc. Jpn.* 70 (1997) 1021–1026.
- [33] R.I. Kaiser, K. Roessler, Theoretical and laboratory studies on the interaction of cosmic-ray particles with interstellar ices. Part I. Synthesis of polycyclic aromatic hydrocarbons by cosmic-ray-induced multicenter mechanism, *Astrophys. J.* 475 (1997) 144.
- [34] B.C. Clark, L.W. Mason, J. Kissel, Systematic of the “CHON” and other light element particle populations in comet P/Halley, *J. Astron. Astrophys.* 187 (1987) 779–784.
- [35] M.V. Gerasimov, L.M. Mukhin, E.N. Safonova, The formation of organic substances under fast evaporation of meteorites and minerals, *Bull. Russian Acad. Sci., Geology (Izvestiya Akademii Naukseriya Geologicheskaya)* 4 (1991) 119–126 (in Russian).
- [36] S.S. Prasad, S.P. Tarafdar, UV radiation field inside dense clouds: its possible existence and chemical implication, *Astrophys. J.* 267 (1983) 603–609.
- [37] P. Ehrenfreund, S.B. Charnley, From Astrochemistry to Astrobiology, First European Workshop on Exo/Astrobiology, Frascati, EPA SP-496, 2001, pp. 35–42.
- [38] R.I. Bickley, Heterogeneous photocatalysis, *Catalysis* 2 (1978) 87–106.
- [39] N. Serpone, A. Salinaro, A.V. Emeline, V.K. Ryabchuk, Turnovers and photocatalysis: a mathematical description, *J. Photochem. Photobiol. A: Chem.* 130 (2000) 83–94.
- [40] R.A. Smith, *Semiconductors*, 2nd ed., Cambridge University Press, Cambridge, 1978.
- [41] V.L. Bonch-Bruевич, S.G. Kalashnikov, *Physics of Semiconductors*, Nauka, Moscow, 1990.
- [42] V.L. Vinetckii, G.A. Kholodar, *Statistic Interaction Between Electrons and Defects in Semiconductors*, Naukova Dumka, Kiev, 1969.
- [43] R.S. Knox, *Theory of Excitons*, Academic Press, London, 1963.
- [44] F. Seitz, J. Koehler, Displacement of atoms during irradiation, in: F. Seitz, D. Turnbull (Eds.), *Solid State Physics*, vol. 2, Academic Press, New York, 1956, pp. 307–442.

- [45] S.G. Davison, J.P. Levine, Surface States, in: H. Ehrenreich, F. Zeitz, D. Turnbull, D. (Eds.), Solid State Physics, vol. 25, Academic Press, New York, 1970.
- [46] I.D. Levine, P. Mark, Theory and observation of intrinsic surface states on ionic crystals, *Phys. Rev.* 144 (1966) 751–763.
- [47] M.I. Klinger, Ch.B. Luschik, T.V. Mashovets, M.I. Elango, Defect formation in solids by the decay of electronic excitations, *Usp. Fiz. Nauk* 147 (1985) 523–558.
- [48] Th.Th. Volkenstein, Electronic Processes on Semiconductor Surfaces During Chemisorption, Consultants Bureau, New York, 1991.
- [49] R. Coekelbergs, A. Crucq, J. Decot, A. Frennet, Heterogeneous synthesis of ammonia induced by beta and gamma rays, *J. Chim. Phys.* 60 (1963) 899–901.
- [50] Yu.P. Solonitsyn, I.M. Prudnikov, V.M. Yurkin, Study of memory effect in photostimulated adsorption at metal oxides adsorbents, *Russ. J. Phys. Chem.* 57 (1982) 2028–2030.
- [51] L.L. Basov, G.N. Kuzmin, I.M. Prudnikov, Yu.P. Solonitsyn, Photoadsorption processes at metal oxides, *Usp. fotoniki* 6 (1976) 82–120.
- [52] V.M. Yurkin, Study of memory effect in photostimulated adsorption of molecules at metal oxides, Ph.D. Thesis, Leningrad State University, Leningrad, USSR, 1984.
- [53] A.M. Volodin, V.A. Bolshov, T.A. Konovalova, Photostimulated formation of radicals on oxide surfaces, *Mol. Eng.* 4 (1994) 201–226.
- [54] B.N. Shelimov, B.B. Kasansky, Photochemical processes on supported oxide surfaces, in: K.I. Zamaraev, V.N. Parmon (Eds.), Photocatalytic Conversion of Solar Energy, Nauka, Novosibirsk, 1991, pp. 109–137.
- [55] V.I. Korotkov, V.E. Kholmogorov, Two photon dissociation of water in heterogeneous systems, in: A.A. Krasnovsky (Ed.), Photoexcited Molecules, Nauka, Leningrad, 1982, pp. 176–188.
- [56] P. Pichat, A.M. Herrmann, Adsorption–desorption, related mobility and reactivity in photocatalysts, in: N. Serpone, E. Pelizzetti (Eds.), Photocatalysis: Fundamentals and Applications, Wiley/Interscience, New York, 1989, pp. 217–249.
- [57] A.L. Linsenbiger, L. Guangquan, J.T. Yates, Photocatalysis on TiO₂ principles mechanisms and selected results, *Chem. Rev.* 95 (1995) 735–738.
- [58] A.V. Emeline, E.V. Lobyntseva, V.K. Ryabchuk, N. Serpone, Spectral dependencies of the quantum yield of photochemical processes on the surface of wide band-gap metal oxides. Part II. Gas/solid system involving scandia (Sc₂O₃) particles, *J. Phys. Chem. B.* 103 (1999a) 1325–1331.
- [59] A. Fujishima, T.N. Rao, D. A. Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C* 1 (2000) 1–21.
- [60] N. Serpone, E. Pelizzetti, in: M.D. Archer, A.J. Nozik (Eds.), Solar Photochemical Remediation of Air and Water, Photoconversion of Solar Energy—Photochemical and Photoelectrochemical Approaches, vol. III, Imperial College Press, London, in press (Chapter 17).
- [61] Yu. Gruzdkov, A.E.P. Savinov, V.N. Parmon, Photocatalysis with Dispersed Semiconductors, in: K.I. Zamaraev, V.N. Parmon (Eds.), Photocatalytic Conversion of Solar Energy, Nauka, Novosibirsk, 1991, pp. 138–179.
- [62] Graetzel M. (Ed.), Energy Resources Through Photochemistry and Catalysis, Academic Press, New York, 1988.
- [63] V.K. Ryabchuk, Photoreactions of small molecules at the surface of alkali metal halides, *Catal. Today* 58 (2000) 89–102.
- [64] L.L. Basov, Yu.P. Efimov, Yu.P. Solonitsyn, Searching experiments in photolysis of water in adsorbed state, *Usp. fotoniki* 4 (1974) 12–18.
- [65] L.L. Basov, V.A. Kotelnikov, Yu.P. Solonitsyn, Photodissociation of simple molecules on oxide adsorbents, in: A.A. Krasnovsky (Ed.), Spectroscopy of Phototransformations in Molecules, Nauka, Leningrad, 1977, pp. 228–241.
- [66] I.K. Kikoin (Ed.), Tables of Data in Physics, Atomizdat, Moscow, 1976, p. 990.
- [67] P. White, K. Zimmermann, Spectroscopic studies of interstellar clouds, *J. Astrophys.* 227 (1979) 824–831.
- [68] J.H. De Boer, Elektronnaya Emissia and Yavleniya Adsorbicii, Leningrad, Moscow, 1936.
- [69] J.H. De Boer, G. Houben, Misleading color reactions, *Proc. Konickl. Nederland. Akad. Wetenschap.* 54 (1951) 421–429.
- [70] A.N. Terenin, Izbrannie Trudi, vol. 3, Nauka, Leningrad, 1975, p. 346.
- [71] V.A. Kotelnikov, A.N. Terenin, Photochemical processes on the surface of aluminum oxide, *Dokl. Akad. Nauk. SSSR* (Reports of Academy of Science USSR) 174 (1967) 1366–1369.
- [72] S.L. Kaliaguine, B.N. Shelimov, V.B. Kazansky, Reactions of methane and ethane with hole centers, *J. Catal.* 55 (1978) 384–393.
- [73] G.N. Kuzmin, M.V. Knatko, S.V. Kurganov, Light and X-ray induced chemistry of methane on TiO₂, *React. Kinet. Catal. Lett.* 23 (1983) 313–317.
- [74] O.B. Kotova, Study of Photoprocesses at Near-Surface Space in Semiconductors and Dielectrics Involving Simple Molecules, Ph.D. Thesis, Leningrad State University, Leningrad, USSR, 1986.
- [75] V.S. Zakharenko, Photoadsorption and photooxidation on metal oxides: components of tropospheric solid aerosols under the earth's atmosphere conditions, *Catal. Today* 39 (1997) 243–249.
- [76] V.B. Kazanskii, Nature of the radiation-induced hole defects on the surface of metal oxides and their role in adsorption and catalysis, *Kinet. Katal.* 19 (1978) 279–291.
- [77] O.V. Krilov, Catalysts and mechanism of oxidative condensation of methane, *Kinet. Katal.* 34 (1993) 13–18.
- [78] J.C. Hemminger, R. Carr, G.A. Somorjai, The photoassisted reaction of gaseous water and carbon dioxide adsorbed on SrTiO₃(1 1 1) face to form methane, *Chem. Phys. Lett.* 57 (1978) 100–104.
- [79] F. Saladin, I. Kamber, K. Pfanner, G. Calzaferri, Photochemical water oxidation to oxygen at solid/gas interface of AgCl on zeolite A, *J. Photochem. Photobiol. A: Chem.* 109 (1997) 47–52.
- [80] G.M. Schrauzer, T.D. Guth, Photolysis of water and photoreduction of nitrogen on titanium dioxide, *J. Am. Chem. Soc.* 99 (1977) 7189–7193.
- [81] M. Schiavello, Basic concepts in photocatalysis, in: M. Schiavello (Ed.), Photocatalysis and Environment, Kluwer Academic Publishers, Dordrecht, 1988, pp. 351–356.
- [82] R.I. Jayanty, R.K.M. Navio, J.A. Bickley, C. Real, M. Macris, Photooxidative fixation of molecular nitrogen on TiO₂ (rutile) surface: the nature of adsorbed nitrogen-containing species, *Surf. Sci.* 251–252 (1991) 1052–1056.
- [83] K.Ya. Kasparov, A.N. Terenin, Optical investigations of activated adsorption. Part I. Photodecomposition of NH₃ adsorbed on catalysts, *Acta Phys. Chem. USSR* 15 (1941) 343–365.
- [84] W.W. Dunn, Y. Aikawa, A.J. Bard, Heterogeneous photosynthetic production of amino acids at Pt/TiO₂ suspensions by near ultraviolet light, *J. Am. Chem. Soc.* 103 (1981) 6893–6897.
- [85] D.E. Woon, Pathways to glycine and other amino acids in ultraviolet-irradiated astrophysical ices determined via quantum chemical modeling, *Astrophys. J.* 571 (2002) L177–L180.
- [86] M.P. Bernstein, J.P. Dworkin, S.A. Sandford, G.W. Cooper, L.J. Allamandola, Racemic amino acids from the ultraviolet photolysis of interstellar ice analogs, *Nature* 416 (2002) 401–403.
- [87] G.M. Munoz Caro, U.J. Meierhenrich, W.A. Schutte, B. Barbier, A. Arcones Segovia, H. Rosenbauer, W.H.-P. Thiemann, A. Brack, J.M. Greenberg, Amino acids from ultraviolet irradiation of interstellar ice analogs, *Nature* 416 (2002) 403–406.
- [88] J.M. Greenberg, J.S. Gillette, G.M. Munoz Caro, T.B. Mahajan, R.N. Zare, A. Li, W.A. Schutte, M. de Groot, C. Mendoza-Gomez, Ultraviolet photoprocessing of interstellar dust mantles as a source of polycyclic aromatic hydrocarbons and other conjugated molecules, *Astrophys. J.* 531 (2000) L71–L73.

- [89] J. Onoe, T. Kawai, S. Kawai, Peptide formation from amino acid with semiconductor photocatalysis, *Chem. Lett. (Jpn.)* (1985) 1667–1670.
- [90] J.P. Ferris, G. Ertem, Oligomerization reactions of rubonucleotides on montmorillonite: reaction of the 5'-phosphorimidazolidine of adenosine, *Science* 257 (1992) 1387–1389.
- [91] V.A. Otroshchenko, N.V. Vasilyeva, A.M. Kopilov, Abiotic formation of oligonucleotides on basalt surfaces, *Orig. Life* 15 (1985) 115–120.
- [92] V.A. Otroshchenko, G.A. Lavrentjev, T.Ph. Strigunkova, Oligonucleotide formation on the mineral surface irradiated with gamma rays, *Stud. Biophys.* 113 (1986) 241–245.
- [93] T.F. Strigunkova, G.A. Lavrentiev, V.A. Otroshchenko, Abiogenic synthesis of oligonucleotides on kaolinite under the action of ultraviolet radiation, *J. Mol. E* 23 (1986) 290–293.
- [94] D.F. Ollis, E. Pelizzetti, N. Serpone, in: N. Serpone, E. Pelizzetti, (Eds.), *Photocatalysis: Fundamentals and Applications*, Wiley/Interscience, New York, 1989, pp. 603–637.
- [95] A.V. Emeline, A.V. Rudakova, V.K. Ryabchuk, N. Serpone, Photostimulated reactions at the surface of wide band-gap metal oxides (ZrO₂ and TiO₂): interdependence of rates of reactions on pressure–concentration and on light intensity, *J. Phys. Chem. B* 102 (1998) 10906–10916.
- [96] A.V. Emeline, V.K. Ryabchuk, N. Serpone, Factors affecting the efficiency of a photocatalyzed process in aqueous metal-oxide dispersions: prospect for distinguishing between the two kinetic models, *J. Photochem. Photobiol. A: Chem.* 133 (2000a) 89–97.
- [97] A.V. Emeline, G.N. Kuzmin, D. Purevdorj, I.G. Shenderovich, Spectral and temperature dependencies of the quantum yield of gases photoadsorption on powdered titania, *Kinet. Katal.* 38 (1997) 446–450.
- [98] G.N. Kuzmin, D. Purevdorj, I.G. Shenderovich, Spectral and temperature dependencies of the quantum yield of photoadsorption of simple gases on dispersed zinc oxide, *Kinet. Katal.* 36 (1995) 790–794.
- [99] A.M. Volodin, A.E. Cherkashin, Study of mechanism of photocatalytic oxidation of carbon monoxide on zinc oxide by ESR. Part I. Formation and stability of CO₂^{•−}: the influence of CO₂ on stabilization of electron and hole centers, *Kinet. Katal.* 22 (1981a) 979–985.
- [100] A.M. Volodin, A.E. Cherkashin, Study of mechanism of photocatalytic oxidation of carbon monoxide on zinc oxide by ESR. Part II. Kinetic mechanism of formation and decay of CO₂^{•−}: double pathway multi-steps scheme of reaction, *Kinet. Katal.* 22 (1981) 1227–1231.
- [101] N.S. Andreev, A.V. Emeline, S. Polikhova, V.K. Ryabchuk, N. Serpone, photoinduced processes in heterogeneous gas–solid systems, temperature dependence of a surface chemical reaction on alumina and the pHCL emission in the solid, *J. Phys. Chem. B*, submitted for publication.
- [102] A.M. Volodin, A.E. Cherkashin, ESR spectrum of methyl radical on ZnO surface, *React. Kinet. Catal. Lett.* 18 (1982) 243–246.
- [103] N. Serpone, G. Sauve, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizzetti, H. Hidaka, Standardization protocol of process efficiencies and activation parameters in heterogeneous photocatalysis: relative photonic efficiencies >ξ_r, *J. Photochem. Photobiol. A: Chem.* 94 (1996) 191–203.
- [104] A.V. Emeline, V.K. Ryabchuk, N. Serpone, Spectral dependencies of the quantum yield of photochemical processes on the surface of nano/micro-particulates of wide band-gap metal oxides. Part I. Theoretical approach, *J. Phys. Chem. B* 103 (1999) 1316–1324.
- [105] A.V. Emeline, A. Salinaro, N. Serpone, Spectral dependence and wavelength selectivity in heterogeneous photocatalysis. I. experimental evidence from the photocatalyzed transformation of phenols, *J. Phys. Chem. B* 104 (2000) 11202–11210.
- [106] P.C. Frisch, J.M. Dorschner, J. Geiss, J.M. Greenberg, E. Grun, M. Landgraf, P. Hoppe, A.P. Jones, W. Kratschmer, T.J. Linde, G.E. Morfill, W. Reach, J.D. Slavin, J. Svestka, A.N. Witt, G.P. Zank, Dust in the local interstellar wind, *Astrophys. J.* 525 (1999) 492–516.
- [107] T. Henkel, T. Stephan, E.K. Jessberger, P. Hoppe, R. Strebel, S. Amari, E.K. Zinner, R.S. Lewis TOF-SIMS analysis of 13 presolar silicon carbide grains, in: *Proceedings of the 65th Meteoritic Society Meeting*, Los Angeles, CA, 2002.
- [108] E. Zinner, S. Amari, R. Guinness, A. Nguyen, F.J. Stadermann, Isotopic compositions of small presolar dust grains, in: *Proceedings of the Goldschmidt Conference*, Davos, Switzerland, 2002.
- [109] A.M. Davis, M.J. Pellin, C.E. Tripa, M.R. Savina, R.S. Lewis, R.N. Clayton, S. Amari, Multielement analyses of single presolar SiC grains from supernovae, in: *Proceedings of the Goldschmidt Conference*, Davos, Switzerland, 2002.
- [110] M.J. Pellin, M.R. Savina, E. Tripa, W.F. Calaway, A.M. Davis, R.S. Lewis, S. Amari, R.N. Clayton, C. N, Si, Fe, Sr, Zr, Mo, and Ba isotopic analyses of type X Murchison SiC grains: experimental evidence for a new type of stellar nucleosynthesis in supernovae, in: *Proceedings of the 65th Annual Meteoritical Society Meeting*, Los Angeles, CA, 2002.
- [111] S. Amari, A. Nguyen, E. Zinner, R.S. Lewis, Multi-element isotopic analysis of presolar graphite fraction KFA1 from the Murchison meteorite, in: *Proceedings of the 65th Annual Meteoritic Society Meeting*, Los Angeles, CA, 2002.
- [112] L.L. Basov, O.B. Kotova, G.N. Kuzmin, V.K. Ryabchuk, Heterogeneous photocatalysis as the path towards the origin of life at primitive earth, in: *Proceedings of the Abstracts of 11th ISSOL Meeting*, Prague, 1989, pp. 57–58.
- [113] J.P. Pinto, G.R. Gladstone, Y.L. Yung, Photochemical production of formaldehyde in the earth's primitive atmosphere, *Science* 210 (1980) 183–185.
- [114] A.C. Lasaga, H.D. Holland, M.J. Dwyer, Primordial oil slick, *Science* 174 (1971) 53–55.
- [115] J.K. Kasting, K.J. Zahnle, J.C.G. Walker, Photochemistry of methane in the early earth's atmosphere, *Precamb. Res.* 20 (1983) 121–148.
- [116] W.G. Filby, M. Mintas, H. Gusten, Heterogeneous catalytic degradation of chlorofluoromethanes on zinc oxide surfaces, *Ber. Bunseng. Phys. Chem.* 85 (1981) 189–192.
- [117] K.M. Sancier, H. Wise, Photoassisted oxidation of organic materials catalyzed by sand, *Atmos. Environ.* 15 (1981) 639–640.
- [118] N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzetti, H. Hidaka, Exploiting the interparticle electron transfer process in the photocatalyzed oxidation of phenol, 2-chlorophenol, and pentachlorophenol: chemical evidence for electron and hole transfer between coupled semiconductors, *J. Photochem. Photobiol. A: Chem.* 85 (1995) 247–255.
- [119] N. Serpone, E. Borgarello, E. Pelizzetti, Utilization of the semiconductor particle as a micro-photoelectrochemical cell: evidence for interparticle electron transfer and application to photocatalysis, *J. Electrochem. Soc.* 135 (1988) 2760–2766.
- [120] N. Serpone, E. Borgarello, M. Gratzel, Visible light-induced generation of hydrogen from H₂S in mixed semiconductor dispersions: improved efficiency through interparticle electron transfer, *J. Chem. Soc. Chem. Commun.* (1984) 342–344.
- [121] R.F. Khairutdinov, N. Serpone, Kinetics of chemical reactions in restricted geometries, *Progr. React. Kinet.* 21 (1996) 1–68.
- [122] Yu.I. Aristov, V.N. Parmon, K.I. Zamaraev, Tunnel recombination of surface and bulk radiation defects in finely dispersed calcium oxide at 4.2 and 77 K, *React. Kinet. Catal. Lett.* 27 (1985) 245–249.
- [123] Yu.I. Aristov, A.I. Volkov, V.N. Parmon, K.I. Zamaraev, Tunneling electron transfer from bulk electron centers of magnesium oxide to adsorbed molecules of nitrous oxide, *React. Kinet. Catal. Lett.* 25 (1984) 329–334.

- [124] Yu.I. Aristov, V.N. Parmon, K.I. Zamaraev, Reactions of electron tunnel transfer on a magnesium oxide surface, *Khim. Fiz.* (1982) 1233–1238.
- [125] A.V. Emeline, G.V. Kataeva, V.K. Ryabchuk, N. Serpone, Photostimulated generation of defects and surface reactions on a series of wide band-gap metal-oxide solids, *J. Phys. Chem. B* 103 (1999c) 9190–9199.



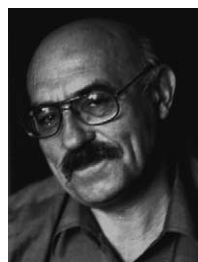
Alexei Emeline was born in 1965 in Karaganda, USSR. He graduated from Tomsk State University (Russia) with a MSc degree in experimental physical chemistry in 1990, and a PhD in molecular physics from the St. Petersburg State University in 1995. He was a research engineer (1991) at Tomsk State University, a junior researcher (1994–1995), researcher (1995–1996) in the Institute of Physics of the St. Petersburg State University, and assistant professor (1996–2000)

in the Department of Physics of St. Petersburg State University. In 1997–1998, he was a NATO science fellow in Department of Chemistry and Biochemistry at Concordia University, Montreal, Canada, under the supervision of Prof. N. Serpone. Currently, he is a DSc fellow of the Department of Physics at St. Petersburg State University and a research associate at Concordia University. His fields of current interests are photophysics and photochemistry of gas/solid and liquid/solid heterogeneous systems, heterogeneous photocatalysis, and photostimulated processes in solids. He has published over 30 articles.



Vladimir Otroshchenko was born in Tashkent, USSR, in 1934. He received his MSc from the Faculty of Physics at Moscow State University in 1958, and his PhD in biology from the Institute of Developmental Biology of the USSR Academy of Sciences, Moscow, in 1969. He was a junior research fellow at the United Institute of the Nuclear Researches, Dubna (1958–1960) and in the Radiobiology Department of the Kurchatov Institute of Atomic Energy, Moscow (1960–1968);

chief of laboratory at the Institute of Space Research, USSR Academy of Sciences, Moscow, from 1968 to 1970; and senior research fellow at the Vernadsky Institute of Geochemistry, USSR Academy of Sciences, Moscow. Since 1972, he has been a research professor at the Bach Institute of Biochemistry, Russian Academy of Sciences, Moscow, which awarded him a full professorship in 1997. He is a member of the Russian Society of Biochemistry; and of the International Society for the Study of the Origin of Life (ISSOL). His research interests are concerned with the origin and evolution of organic and genetic systems, and in chemical and computer studies of the interaction of amino acids and nucleotides with oligonucleotides.



Vladimir K. Ryabchuk was born in 1945 in Leningrad (now St. Petersburg), USSR. He obtained his PhD in 1984 at Leningrad State University (SPSU), Leningrad, Soviet Union. He is currently an associate professor of Physics in the Department of Photonics at St. Petersburg State University, and is head of the Master of Science curriculum "Photonics of Heterogeneous Systems". His fields of interests are in photo-physics and photochemistry of gas/solid interfaces, heterogeneous photocatalysis, and photostimulated processes in solids. He has published over 40 articles and a textbook (with Yu.M. Artem'ev) on the "Introduction into Heterogeneous Photocatalysis" (1999, SPSU). He holds a Soros Docent Award since 2001.



Nick Serpone was born in Toro (CB), Italy, in 1939. He received his BSc Honors in chemistry in 1964 at Sir George Williams University, Montreal, and his PhD in physical inorganic chemistry from Cornell University, Ithaca, NY, in 1968. He has been an assistant professor (1968–1973), associate professor (1973–1980), and professor (1980–1998) at Concordia University. He was a senior research scholar and visiting professor at Boston University (1977–1979); a visiting scientist at the Brookhaven National Laboratory, NY (1979–1981); a visiting professor at the University of Bologna (Italy, 1975–1976), and at the University of Ferrara (Italy, 1997–1998); a Directeur de Recherche au CNRS at the Ecole Centrale de Lyon (France, 1990–1991); and a professeur Invité at the Ecole Polytechnique Fédérale de Lausanne (Switzerland, 1983–1984). He was the founder and director of the Center for Fast Laser Spectroscopy at Concordia University (1981–2000), and from 1987 to 1996, he was a consultant for 3M at Corporate Research Center, USA. He is an associate editor of the Journal of Advanced Oxidation Technologies (since 1994). From 1998 to 2001, he was program director for inorganic, bioinorganic and organometallic chemistry in the Chemistry Division of the National Science Foundation, Washington. He is currently a university research professor and professor emeritus at Concordia University (since 1998). In 1997, he received (with Mel Sahyun and Boris Levy) the Best Paper Award in the Journal of Imaging Science & Technology from the Society for Imaging Science & Technology. He has published over 320 articles and four books, and holds one patent. His research interests are in photochemistry—specifically in heterogeneous photochemistry and photocatalysis of liquid/solid and gas/solid systems as applied to environmental remediation and sunscreens, in semiconductor photophysics and photochemistry, in laser spectroscopy, and in the photochemistry of nanomaterials.