http://dx.doi.org/10.1007/978-3-642-11274-4

TITLE (Entry Type: Long Entry)* PHOTOCHEMISTRY

Your Address

John H. Black

Chalmers University of Technology

Onsala Space Observatory

SE-43992 Onsala, Sweden

John.Black@chalmers.se

Synonyms

Keywords

Definition

Photochemistry refers to the processes by which energy is transferred from electromagnetic radiation (in practice mainly ultraviolet and visible light) into chemical activity in gases, solid particles, and living matter. Photochemical processes partly control the initial conditions for the formation of stars and planets, they may leave traces of the early chemical evolution of planetary systems in the abundances of isotopes, they regulate the input of stellar energy into atmospheres of planets, and they play important roles in the chemistry of living organisms on Earth.

Overview

The origin of life, indeed the origin of structure in the Universe, can be described broadly as a struggle by microscopic processes to overcome the general tendency toward equilibrium. Photochemical processes are very effective in driving a creative dis-equilibrium. Consider complex systems where no single temperature characterizes the physical and chemical state. For example, visible and near-infrared radiation from the surface of the Sun at an effective temperature of 5800 K reaches the atmosphere, oceans, and solid surface of the Earth, which achieves a balance between absorbed and re-radiated energy at an average temperature (<300 K) very conducive to the chemistry of life. The corona of the Sun radiates an intensity of ultraviolet light that greatly exceeds what is expected from a 5800 K blackbody. The ultraviolet sunlight penetrates only the upper layers of our atmosphere, where it interacts with molecules through various quantum processes. The physical and chemical states of these upper layers must be analyzed in terms of the rates of individual microscopic processes, in contrast to the troposphere, which is well mixed and close to local thermodynamic equilibrium. Photodissociation of an oxygen molecule by a quantum of UV light produces free atoms $O_2 + \gamma \rightarrow O + O$, some of which then associate with a molecule to form ozone O_3. Occasionally (but with a known average

* Word range of Entry: approx. 1,650 words excl. references, as agreed with the Editors-in-Chief

probability) an ozone molecule meets a free hydrogen atom (typically a daughter born of the photodissociation of water): the result is a reaction $O_3 + H \rightarrow OH^* + O_2$ in which the product hydroxyl, OH, is formed preferentially in highly excited vibrational states. The internal energy of excited OH is so far out of equilibrium with its surroundings that it is likely to produce several infrared photons rather than to share its excess energy with neighboring molecules in a dance toward thermal balance. These photons produce an airglow that would illuminate our way at night if we had infrared-sensitive eyes. As it is, the infrared airglow nearly blinds sensitive infrared detectors on astronomical telescopes. If this airglow radiation were excited by thermal processes it would be characterized by temperatures of 1000 K or more, in contrast to the 200 K temperature prevailing at 90 km altitude where the ozone-plus-hydrogen source maximizes.

Basic Methodology

The study of photochemistry in astrophysics and planetary science is severely dependent upon theory and experiment in molecular physics and physical chemistry owing to the need for vast amounts of data on fundamental processes like photodissociation, photoionization, and two-body chemical reactions. In the interstellar clouds that collapse to form stars, protoplanetary disks, and eventually planets, the most abundant gaseous molecules are H_2 and CO, yet the heating and cooling processes are partly controlled by other minor species, like atomic C, C^+, and O, which arise directly from the photochemistry of CO. The surfaces of interstellar clouds (and some layers of planet-forming disks) are exposed to ultraviolet starlight that typically has an abrupt cutoff at the wavelength of the Lyman limit of atomic hydrogen, 91.2 nm. These surface layers, called photon-dominated regions (PDR), exhibit a rich photochemistry far out of equilibrium. Both H_2 and CO are special in that they are photodissociated via line absorptions that easily become saturated leading to self-shielding, whereas most other molecules are photodissociated in continuous absorption processes and shielded mainly by the absorption and scattering by dust particles. In CO, the photodissociation can be isotope-selective in the sense that the less abundant isotopologues $^{13}C^{16}O$ and $^{12}C^{18}O$ are more readily broken apart than the most common form $^{12}C^{16}O$. At low temperatures, <50 K, this effect competes with a temperature-sensitive ion-exchange reaction $^{13}C^+ + {}^{12}CO \leftrightarrow {}^{12}C^+ + {}^{13}CO$, which tends to enhance the abundance of the rarer species. It has been suggested that isotope-selective photodissociation of CO in the protoplanetary disk of the immature solar system might account for abundance anomalies in oxygen isotopes that have persisted in meteorites to the present time. This would seem to be plausible, however, only if carbon monoxide had been the main reservoir of oxygen. The initial conditions for star-formation may be set in gas and dust at temperatures of 10 K where the density is of the order of 10000 hydrogen molecules cm^{-3}. In the centers of these dark clouds where no starlight penetrates, one might expect no photochemistry; however, the cosmic rays (mainly protons with energies greater than 10 MeV) ionize hydrogen and the resulting fast electrons lose significant energy by exciting other hydrogen molecules to radiate ultraviolet photons. This internal source of radiation, known as the Prasad-Tarafdar mechanism, adds significant photochemical activity to what is driven directly by cosmic-ray ionizations. Cosmic rays are perhaps the most extreme example of a non-thermal, dis-equilibrating agent. Photochemistry regulates the abundances of ions and free electrons in the mostly neutral material of star-forming clouds and planet-forming disks. These charged particles in turn couple the magnetic field to the gas and thus mediate the effects of magnetic forces, rotation, and gas flows in the early evolution of stars and planets.

Once a planetary system has formed, photochemistry operates in many ways. For example, Saturn's largest satellite, Titan, has a thick nitrogen-methane atmosphere (surface pressure 1.5 bar) with a rich organic photochemistry. Photochemical models of Titan's atmosphere have become increasingly sophisticated in response to the Voyager and Cassini/Huygens missions. One key point about Titan is that photoionization of N_2 by extreme-ultraviolet sunlight is more effective than photodissociation, so that $N_2^+ + CH_4 \rightarrow CH_3^+ + H + N_2$ initiates an ion-driven photochemistry. As a result, the ionosphere must be considered together with the neutral atmosphere, and transport mechanisms complement the basic microscopic chemical processes.

In the coming years, as atmospheres of extra-solar planets become better observed, there will be increasing recognition of the role of photochemistry in their structures and evolution. There are already indications that the abundances of stable molecules like CH_4, CO_2, CO, and H_2O depart from equilibrium at pressures above 1 bar in the atmosphere of exoplanet HD 189733b. Photochemistry can affect atmospheric dynamics and evolution through photodissociation processes that yield kinetically hot product atoms and molecules.

It is widely thought that photochemistry has played an important role in the origin of life on Earth and in the subsequent impact of living organisms on the physical evolution of the terrestrial atmosphere. An oxygen-rich atmosphere is one consequence of our inhabited planet, where photosynthesis in plants has been operating. Strategies for astronomical searches for evidence of life elsewhere can be evaluated in relation to the spectrum and photometric variability of earthshine, the reflected light of Earth as seen from outside. The reflectance spectrum of terrestrial vegetation has a sharp edge at 700 nm wavelength, although this may be neither a universal nor unique signature of life on planets.

Key Research Findings

[Please enter your text here …]

Applications

[Please enter your text here …]

Future Directions

[Please enter your text here …]

See also

key words to flag for cross-references:
exoplanets/extrasolar planets
atmosphere
ionosphere
Titan

comets
interstellar clouds
protoplanetary disks

References and Further Reading

Good general references to the contexts of photochemistry are, for interstellar matter

Lequeux, J. 2005, *The Interstellar Medium*, (Berlin: Springer-Verlag)

and for planetary systems

de Pater, I., Lissauer, J. J. 2010, *Planetary Sciences*, 2nd edition, (Cambridge, UK: Cambridge University Press).

Examples of photochemistry mentioned above are described in the following articles:

Arnold, L. 2008, *Space Science Reviews*, **135**, 323, "Earthshine Observation of Vegetation and Implication for Life Detection on Other Planets".

Gredel, R., Lepp, S., Dalgarno, A., Herbst, E. 1989, *Astrophysical Journal*, **347**, 289, "Cosmic-ray-induced photodissociation and photoionization rates of interstellar molecules".

Grenfell, J. L., Rauer, H., Selsis, F., et al. 2010, *Astrobiology*, **10**, 77, "Co-Evolution of Atmospheres, Life, and Climate".

Krasnolposky, V. A. 2009, *Icarus*, **201**, 226, "A photochemical model of Titan's atmosphere and ionosphere".

Line, M. R., Liang, M. C., Yung, Y. L. 2010, *Astrophysical Journal*, **717**, 496, "High-temperature photochemistry in the atmosphere of HD 189733b"

Röllig, M., Abel, N. P., Bell, T., et al. 2007, *Astronomy & Astrophysics*, **467**, 187, "A photon dominated region code comparison study".

Visser, R., van Dishoeck, E. F., Black, J. H. 2009, *Astronomy & Astrophysics*, **503**, 323, "The photodissociation and chemistry of CO isotopologues: applications to interstellar clouds and circumstellar disks".