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Application of Photochemistry Principles, Models, and Simulations in the Study of Gaseous Components of Space Bodies and Interstellar Matter with Recent Developments

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Abstract: Space exploration was from its inception multidisciplinary field of research. Whether it is a design of devices that separate light into it different wavelengths, comparison of extracted data to known characteristics of spectrum of molecules, engineering of complex autonomous system of interplanetary probes or intricate calculations of vehicle trajectories, the objective was the same, understanding of the Universe around us. Chemistry as fundamental natural science finds its place in the area known as astrochemistry. When it comes to direct experimentation most of work is done on board the remotely operated space probes that are often self-enclosed laboratories on other space objects or orbiters. However, data collected by these is overshadowed by sheer volume of information extracted from light collected by Earth and space-based observatories and it is here that photochemistry takes the prime role. In last few decades, with development of computing technology, mathematical models have taken root in interpreting data collected by observations and predicting the characteristics of objects analogous to already well-studied ones. Several of the recent studies in this field have been discussed in this paper.

INTRODUCTION

Astrochemistry is a theoretical study of chemical processes in cosmic environments and the observational determination of physical parameters through the study of abundances of molecular species (Meyers, 2001). As such astrochemistry is a unique three-way bridge between chemistry, physics, and astronomy that enables the study of complex environments and potential ecosystems. With one of the main aims of space exploration being search for life beyond Earth, astrochemistry play a key role in that endeavor by detection and classification of present compounds and their interactions in different environments ranging from cometary surfaces and coma to vast planetary and interstellar nebulae that may lead to formation of new stars, planets and other space bodies. (Meyers, 2001)

Astrochemistry is unique in area of space exploration due to fact that scientists can actually conduct meaningful sampling, analysis, and experimentation with samples from space objects. These samples come from a manned Lunar mission conducted during the third quarter of 20th century and from a variety of unmanned probes sent mostly to Mars, but also as far as Jupiter, Saturn and their respective moons and comets. The experimentation on collected samples is mainly conducted onboard the probes, with few of samples of smaller bodies, mainly comets and

asteroids, being delivered to laboratories on Earth. (Meyers, 2001)
Photochemistry is a branch of chemistry that deals with the interaction of atoms and molecules with light and its effects on chemical reactions. This type of research is especially common in the study of space objects as the great majority of information comes from analysis of light gathered by telescopes. (Shaw, 2006)

EXPERIMENTAL ASPECTS

The observational segment of study is conducted mainly in the range of infrared and millimeter wavelengths. Relatively cold parts of the universe radiate in IR spectrum. The same is true for the very far red-shifted objects. As Earth's atmosphere absorbs a significant part of IR spectrum, it is necessary to establish space observatories that do not face this. As Earth's atmosphere is transparent to millimeter wavelengths, observation in this regime are almost exclusively conducted from the surface. (Lewis, 2004; Rau, 2002; Herwit, 2006)

Figure 1: Herschel space observatory; Credit: ESA/ AOES Medialab; background: Hubble Space Telescope image (NASA/ESA/STScI)

Herschel Space Observatory was ESA project that was active between 2009 and 2013 and among its main aims was a study of molecular chemistry in the Universe and observation of the chemical composition of atmospheres of the objects in the Solar system. With its rather wide range of wavelengths of 55 to 672 µm, far infrared and submillimeter range, it was well suited for this task, especially for the study of simple organic molecules and their interactions. The light collected by its 3.5 meter wide primary mirror was channeled and processed in its 3 instruments. (http://sci.esa.int/herschel/; Smith, 2013)

Instruments used in Herschel

PACS (The Photodetector Array Camera and Spectrometer) is one of the three science instruments on ESA's far-infrared and submillimeter observatory. It employs two Ge:Ga photoconductor arrays with 16x25 pixels, each, and two filled silicon bolometer arrays with 16x32 and 32x64 pixels, respectively, to perform integral-field spectroscopy and imaging photometry in the 60-210 µm wavelength regime. (Poglitsch, 2003)
SPIRE (Spectral and Photometric Imaging Receiver) is a system of 2 instruments: an imaging photometer with broad bands on 250, 350 and 500 µm and a two-band Fourier-Transform imaging spectrometer covering 194-318 µm and 294-671 µm.
(https://www.cosmos.esa.int/web/herschel/spire-overview)
HIFI (The Heterodyne Instrument for the Far Infrared) is a heterodyne spectrometer with high resolution that operates by mixing incoming signals with a locally generated reference monochromatic signal and extracting frequency difference and processes it further. HIFI consists of seven separate local oscillators covering two bands from 480-1250 GHz and 1410-1910 GHz.
(http://sci.esa.int/herschel/41327-hifi-instrument/)
Following its orbital insertion, the Cassini spacecraft became Saturn's first artificial satellite and during its years of operation, it has compiled a large amount of data on its atmosphere structure and composition, its vast rings and satellites. In addition to the study of Saturn, one of the main objectives of Cassini mission was a study of Saturn's moon Titan. During the course of its mission, Cassini has made about 40 flybys close to Titan and has deployed a robotic probe called Huygens to its surface. During its descent, onboard instruments have collected a large amount of data on its atmospheric composition and meteorology. While the collection of data during descent was the main goal, the probe, somewhat surprisingly, survived the landing on Titan's surface and has sent further data and pictures of moon's surface. (Coustenis, Taylor, 2008)

Figure 2: Cassini spacecraft; Credit: NASA/JPL-Caltech

The Doppler Wind Experiment (DWE) was designed to determine the direction and strength of Titan's zonal winds and was carried out in the Huygens mission which was ESA's contribution to the Cassini/Huygens mission to the Saturn and Titan. The main goal of DWE was the high accuracy and resolution determination wind velocities up to 160 kilometers from surface, with the secondary goal being determination of spectral characteristics of turbulences and wave activities with measurement of Doppler fluctuations. This achieved by the use of oscillators located in both Huygens probe as well as Cassini spacecraft. DWE completed remote-sensing observations of temperature and wind from Cassini Orbiter providing us with information about zonal wind using Composite Infrared Spectrometer (CIRS) experiment. (http://sci.esa.int/cassini-huygens/31193-instruments/?fbodylongid=735)

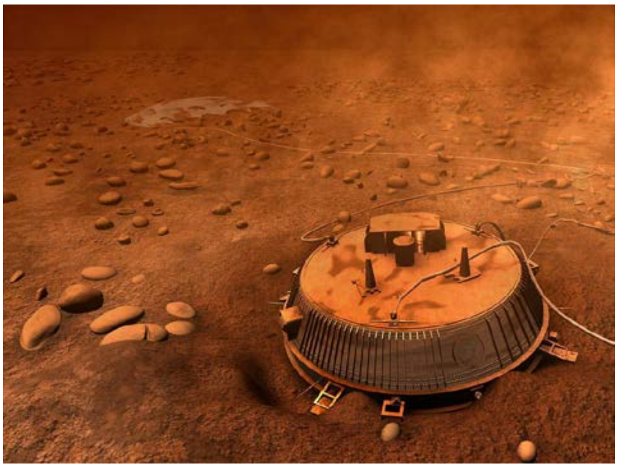

Figure 3: Huygens probe; Credit: Credit: ESA

The largest and probably most well-known and productive millimeter/submillimeter regime observatory is the astronomical interferometer complex located in the Atacama Desert in Chile, the Atacama Large Millimeter/submillimeter Array or ALMA, constructed and operated by European Southern Observatory and National Radio Astronomy Observatory. Among most significant discoveries made by ALMA was the detection of molecules of water, ammonia and methanol in interstellar space that was previously thought to be almost exclusively hydrogen and dust. It is now shown that molecules can be created in reaction to dust grains that can lead to further reactions to form more complex organic compounds. (http://www.almaobservatory.org)

DISCUSSION FOR SOME SPACE BODIES

Atmospheres of space bodies significantly vary depending on type and size of the object, its location relative to its parent star as well as its evolution. Generally, the majority of atmospheric masses are simple molecules, with more complex ones and noble gases being present in traces. However, as each molecule has its unique fingerprint in the electromagnetic spectrum, mostly in IR and submillimeter range, it is possible with instruments of sufficient sensitivity to detect these patterns and therefore to some extent deduce the atmospheric compositions.

Comets are objects that are made up of nucleus and coma. The nucleus is composed of mostly rocks, frozen water and gases such as carbon oxides, methane and ammonia and are also shown to contain various organic compounds such as simple hydrocarbons, alcohols, and aldehydes. Comets in Solar system mostly follow highly eccentric orbits around Sun and once they approach it the frozen and trapped gases and dust are released forming cometary coma that reflects Sun’s light. As comets albedo (amount of light reflected by an object) is quite small they are mostly visible only when vast clouds of coma are formed, that are also known as comet’s tail. The very fact that cometary albedo is small was deduced to be due to the presence of organic molecules on cometary nucleus surfaces (Morison, 2008).

Venus is a second planet from the Sun, it is similar in size to Earth but quite different in atmospheric aspects, mainly due to the fact that it is composed of carbon dioxide, small amount of nitrogen with other gases mostly in trace amounts, such as nitrogen oxides, and sulfur dioxide for which the content is shown to significantly vary in relation to the location and time which is presumed to be due to volcanic activity. Its atmosphere is 93 times larger in mass than Earth's which leads to surface pressure to be over 92 bar. It is also presumed that atmospheric and meteorological factors can lead to rains of acid in the upper atmosphere which however cannot reach the surface in the liquid form due to the high surface temperatures of over 730 K (Morison, 2008).

While Saturn is one of the most spectacular views through the telescope, it is no less interesting in a scientific sense. It is a gas giant positioned as a sixth planet from the Sun and it is shown that it is composed mostly of molecular hydrogen and helium, with smaller percentages of simple organic molecules like methane, ammonia, etc. (Morison, 2008)

Titan, as the largest moon of Saturn, was for a long time target of many observations and studies, with most recent being Cassini-Huygens mission robotic mission. Studies have shown that Titan’s atmosphere contains a significant amount of organic molecules including hydrocarbons and nitriles, generally considered to be created from methane and nitrogen contained in the Titan’s atmosphere. Cassini-Huygens is instrumental in these discoveries with providing a large amount of data regarding chemistry in the atmosphere and Titan’s seasonal characteristics. Titan’s atmosphere is not in the chemical equilibrium, in fact it is a chemical factory that initiates the formation of significant amounts of complex positive and negative ions, UV radiation, energetic ions, and electrons. (Coustenis, Taylor, 2008; Elkins-Tanton, 2006; Gargaud, Amils, Quintanilla, et al., 2006; Coustenis, 2016)

RECENT DEVELOPMENTS IN PHOTOCHEMISTRY

In recent years, a lot of research has been done on photochemical models of Titan's atmosphere. That is because of the feature of Titan to be the only moon in the solar system to have a dense atmosphere. In designing these models, researchers are trying to learn more about the composition of the atmosphere and that data can be used to investigate hazy exoplanets detected by telescopic surveys. Lara et al. (2014) made a time-dependent photochemical model of Titan’s atmosphere to calculate effective lifetimes and the response of Titan’s oxygen compounds to changes in the oxygen input flux. Hickson et al. (2014) made a detailed photochemical model of sulfur compounds in the Titan's atmosphere. These connect hydrocarbon, nitrogen, oxygen, and sulfur chemistries. The results mostly concern the substances that are produced in a specific part of the atmosphere. In the upper Titan's atmosphere, photochemical processes produce mainly CS and H_2CS and C_3S, H_2S and in the lower atmosphere

CH_3SH. Having modeled the atmosphere content, other data about detected exoplanets can be extrapolated by referencing known variables. This is quite useful as most current telescopes do have sufficient strength to resolve subtle characteristics. This is expected to change with the deployment of James Webb Space telescope that is designed to study, among others, atmospheric characteristics and possibly direct imaging of exoplanets that should be an excellent test for current models and the basis for corrections and improvements. Regarding simulation, Titan's photochemistry of atmosphere was simulated using infrared analysis (Couturier-Tamburelli et al., 2015). They came to a result that in Titan's atmosphere, the cyanoacetylene class of molecules would condense first, followed by the dicyanoacetylenes which leads to fractionation of different class of molecules. Titan is uniquely useful in photochemical research as large amount data about it has been obtained by *Cassini* orbiter and Huygens Lander. Also, there was an attempt to construct a numerical model of Titan's atmosphere (Zhu, Strobel, 2007). It gives an insight into some of the physical characteristics concerning transport and photochemistry of Titan. It also stimulates further research that could enrich the observations by *Voyager* and *Cassini* spacecraft.

Similarly, other planets' atmospheres are modeled. Some researchers tried to model specific compounds that atmosphere contains in order to study it deeper. Mills et al. (2011) were working on a photochemical model of NOx on Venus. These were preliminary simulations that resulted in the conclusion that odd nitrogen chemistry has significant effects on specific aspects of SO and SO_2 abundances at 80-90 km altitude, but the overall effects from the observed NO abundance are small. It is left for further research to investigate other situations where odd nitrogen chemistry could have more influence as well as additional measurement of NO on Venus. The pseudo 2D chemical model was made by Agúndez et al. (2013) and applied to exoplanets HD 209458b and HD 189733b. Chemical model in this situation is very useful because hot Jupiters do not have an analogue in our solar system so a model provides an insight into their atmospheres. Other reason is that there is a lot of hot Jupiter exoplanets discovered, but very little is known about them. During modeling, thermochemical kinetics, photochemistry, vertical mixing, and horizontal transport were considered. Sub-millimeter spectroscopy was used to investigate trace gas composition of Saturn's atmosphere (Fletcher et al., 2011). Specifically, the method used was Fourier transform spectroscopy from the Herschel/SPIRE (Spectral and Photometric Imaging Receiver) instrument. The data were compared for consistency with Cassini data. They came to several results. Saturn's disk is quasi-isothermal.

Also, there is a certain amount of research dedicated to the interstellar medium and different methods are used. One of them is of Paardekooper et al. (2016) in which a new measurement concept is presented for determining photodesorption rates. These are used to quantify the role that light has on the content of gas and solid stateparticles in nebulae. It was demonstrated on CO ice and the result was that photodesorption rate of CO ice at 20 K is $(1.4\pm0.7)10^{-3}$ molecules per incident vacuum ultraviolet (VUV) photon. As it is well established that CO often is present in significant amounts in nebulae, it was useful for testing in laboratory conditions as it is quite easy to manipulate. The studies were conducted mostly with IR and mass spectrometry-based methods. The measurements made can be used to make a model for comparing the photodesorption rates of CO extrapolated from astronomical data with a model to ascertain the content of the observed area of space. Other method is chemical modeling. Example of such research is reported by Bovino et al. (2016) where three-dimensional hydrodynamic simulations of galaxies were made in order to test effects of key parameters such as metallicity, radiation, and non-equilibrium versus equilibrium metal cooling approximations on the transition between the gas phases in the interstellar medium by using a public chemistry package KROME. Considering very detailed work involving a very broad range of temperatures used in the model including cooling functions, heating and photochemical processes relevant for the study under investigation, it can be concluded that complete model and simulation was designed useful for applications in examining galaxies in the future which was also one of the aims of this research.

Use of mathematics and computers in research is more and more frequent in past years to either help in solving scientific problems or give different perspective to problems in question. That is also the case for photochemistry and we reference to this field of study as computational photochemistry. Ziegler (2015) worked on magneto-gasdynamical simulations implemented using NIRVANA code. It is done by constructing a partial differential equation that describes the chemical kinetics, separating advection and reaction part of the process using second-order Strang-splitting and solving a correspondent system of ordinary differential equation using fourth-order generalised Runge-Kutta method. Proper validations and tests were carried out and it was assured that time-dependent simulation that was done is adequate to successfully handle astrochemical processes. More specific research was done by Bisikalo et al. (2014) in which Monte Carlo simulation was used in order to model oxygen photochemistry in cometary atmospheres. Metastable O(1D) and O(1S) species was considered by computing the energy distribution functions (EDF) and red and green spectral line shapes were obtained. The model is tested on the atmospheres of comets C/1996 B2, Hyakutake and 103P/Hartley 2. The result was that both species investigated had a severely non-Maxwellian EDF which led to broad spectral lines and the suprathermal broadening dominates due to the expansion motion.

CONCLUSIONS

Creation of credible models in astrochemistry and the increasing viability was and is still being fueled by advancements in computer technology and accumulation of data from observations and direct or indirect experiments that are being incorporated in existing models with the aim of improving the end results. As analysis of chemical composition and content of distant objects is very difficult, due to limitations in available instruments, and often yields results of insufficient accuracy, it is possible to use data obtained from well studies objects to construct models of environments which in turn can be used to extrapolate information about objects whose basic characteristics are analogous to known ones. Computer modeling while accurate in its execution of algorithms, is significantly limited by a large number of variables that are difficult to accurately model and therefore existing frameworks are continuously being updated as new data available.

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Summary/Sažetak

Istraživanje svemira je od svog početka bilo multidisciplinarno područje istraživanja. Bilo da je u pitanju dizajn uređaja koji razdvajaju svjetlost na različite talasne dužine, usporedba dobivenih podataka s poznatim karakteristikama spektra molekula, inženjering kompleksnih autonomnih sistema međuplanetarnih sondi ili složenih proračuna putanja letjelica, cilj je bio isti, razumijevanje svemira oko nas. Hemija kao fundamentalna prirodna nauka pronalazi svoje mjesto u području poznatom kao astrohemija. Kada je u pitanju izravno eksperimentiranje, većina istraživanja se obavlja na daljinski upravljanim sondama, koje su često zatvorene laboratorije na drugim svemirskim objektima, ili orbiterima. Međutim, ovako prikupljeni podaci su zasjenjeni količinom informacija prikupljenih analizom svjetlosti koju su sakupljale opservatorije bazirane na Zemlji ili van nje, a ovdje fotohemija igra važnu ulogu. U posljednjih nekoliko decenija, s razvojem računarske tehnologije, matematički modeli su uzeli korijen u tumačenju podataka prikupljenih promatranjima i predviđanjem karakteristika analognih objekata koji su već dobro proučeni. U ovom radu su razmatrana nedavna istraživanja iz ovog područja.