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Laboratory Studies of Methane and its Relationship to Prebiotic Chemistry

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Abstract

In order to examine how prebiotic chemical evolution took place on the Earth prior to the emergence of life, a series of laboratory experiments have been conducted since the 1950s. Methane has been one of the key molecules in these investigations. In earlier studies, strongly reducing gas mixtures containing methane and ammonia were used to simulate possible reactions in the primitive atmosphere of Earth, producing amino acids and other organic compounds. Since Earth's early atmosphere is now considered to be less reducing, the contribution of extraterrestrial organics to chemical evolution has taken on an important role. Such organic molecules may have come from molecular clouds and regions of star formation that created protoplanetary disks, planets, asteroids and comets. The interstellar origin of organics has been examined both experimentally and theoretically, including laboratory investigations simulating interstellar molecular reactions. Endogenous and exogenous organics could also have been supplied to the primitive ocean, making submarine hydrothermal systems plausible sites of the generation of life. Experiments simulating such hydrothermal systems where methane played an important role have consequently been conducted. Processes occurring in other solar system bodies offer clues to the prebiotic chemistry of Earth. Titan and other icy bodies, where methane plays significant roles, are especially good targets. In the case of Titan, methane is both in the atmosphere and also in liquidospheres composed of methane and other hydrocarbons, and has been studied in simulation experiments. This paper reviews the wide range of experimental work modeling these various terrestrial and extraterrestrial environments, and examines the possible role of methane in chemical evolution.

1. Introduction

How life on Earth emerged is one of the largest questions left unanswered. In the 1920s, Oparin and Haldane independently published their idea on the generation of life. It has been referred to as the chemical evolution hypothesis, where life was born after evolution of organic materials dissolved in the primitive ocean. The processes of chemical evolution were, however, considered too difficult to be examined by experiments in the early 20th century.

Miller (1953) reported the first successful abiotic synthesis of amino acids by spark discharges in a gas mixture of methane, ammonia, hydrogen and water, which showed that the chemical evolution hypotheses could be tested. In the 1950s-1970s, a large number of experiments simulating reactions in primitive Earth atmosphere were conducted (Miller and Orgel, 1974). In most of the studies, strongly reducing gas mixtures containing methane and ammonia as major constituents were used as starting materials. In addition to spark discharges, energy sources such as ultraviolet light (Sagan and Khare, 1971), thermal energy (Harada and Fox, 1964), ionizing radiation (Ponnamperuma et al., 1963) and shock waves (Bar-Nun et al., 1970) were used, and successful syntheses of amino acids and/or nucleic acid bases were reported.

Planetary explorations in the late 20th century brought us novel information on formation of the solar system including Earth, which suggested that the primitive Earth atmosphere was never strongly but only slightly reducing (Matsui and Abe, 1986a, b; Kasting, 1990). Major gases in this case would be carbon dioxide and nitrogen, together with some reducing gases such as carbon monoxide, and hydrogen as minor components (Kasting, 1993). If so, prebiotic synthesis of amino acids and other bioorganic compounds would have been quite difficult. For example, only small amounts of amino acids were formed when a gas mixture of carbon dioxide (or carbon monoxide), nitrogen and water was subjected to spark discharges unless high concentration of hydrogen was added to the mixture (Schlesinger and Miller, 1983). However, amino acid formation from atmospheres without methane and ammonia could be still possible if high-energy particle irradiation from cosmic rays and high temperature plasmas, simulating bolide impact of meteorites, were used. Production of amino acid precursors and nucleic acid bases was reported from a mixture of carbon dioxide, carbon monoxide, nitrogen and water with such particle bombardment (Kobayashi et al., 1990; Miyakawa et al., 2002).

On the other hand, a wide variety of organic compounds have been detected in extraterrestrial environments. Interstellar organic molecules have been identified in dense clouds by infrared and/or microwave telescopes for many decades (Herbst and van Dishoeck, 2009), and organic molecules were directly detected with mass spectrometers onboard spacecraft in bodies such as comets (Goesmann et al. 2015), Jupiter (Nixon et al., 2007; Sada et al., 2007) and Titan (Vuitton et al., 2007; Cravens et al., 2006). Extracts from carbonaceous chondrites have been comprehensively analyzed, and a great number of amino acids and some nucleobases were identified together with hydrocarbons, carbonic acids, amines and other organic compounds (Martins et al. 2008; Botta et al. 2008). These extraterrestrial organic compounds have been considered to be important building materials for the first life on Earth. How were organic compounds found in comets and meteorites formed? One of the plausible sites is the interstellar medium. As will be discussed in Section 2, a variety of experiments simulating reactions in interstellar environments have been conducted in which organic compounds were formed.

After delivery of extraterrestrial organic compounds by asteroids, meteorites, comets and/or interplanetary dust particles (IDPs) to primitive Earth, further chemical evolution towards the generation of early life probably took place in the primeval ocean. The perception of the primitive ocean has drastically changed after the discovery of submarine hydrothermal vents in the late 1970s. Submarine hydrothermal systems (SHTSs) have been considered sites for generation of early life on earth for several reasons (Hennet *et al.*, 1992). One of them is that the SHTSs could maintain reducing environments even on present Earth, since reducing gases including methane, ammonia, hydrogen and hydrogen sulfide are quite rich in the hydrothermal fluids. Another reason for being related to the origin of life is that microorganisms have been found in the vents from the phylogenetic tree, close to the last common universal ancestor (LUCA), They are also thermophiles that can grow around 100°C (Pace, 1991).

In Section 3, laboratory experiments simulating SHTS environments are discussed. Two types of experiments have been conducted: those with closed systems by the use of autoclaves, and those with flow systems. A wide variety of organic compounds have been abiotically synthesized from molecules found in SHTSs such as methane. Possible chemical evolution from amino acids or their precursors to peptide and organic aggregates / globules in SHTSs has been suggested.

Though methane is no longer regarded as a plausible major constituent in a primitive Earth atmosphere, it could have been a minor component in it. Titan, the largest Kronian satellite, has a dense atmosphere, where nitrogen is the dominating species (more than 90 %) followed by methane (a few %). Titan is called a natural laboratory of chemical evolution, where various reactions between nitrogen and methane are taking place triggered by solar ultraviolet light and the impact of magnetospheric electrons, meteor impacts and cosmic radiation. In addition, lakes of liquid hydrocarbons have been found on the surface of Titan. Chemical evolution in hydrocarbon solvents, not in water, has been also examined by simulation experiments. In Section 4 we will review such simulation experiments, and discuss the possible generation of life on Titan and its relevance to that on primitive Earth.

In the final Section, we discuss the significance of simulation experiments as a guide for possible reaction pathways toward the generation of life on Earth, and map out future prospects.

Our paper is part of a series of review articles in this journal about methane chemistry in the interstellar medium, planetary and satellite atmospheres and hydrothermal systems at ocean floors. The article is the outcome of the project “The Methane Balance: Formation and Destruction Processes on Planets, Their Satellites, and in the Interstellar Medium.” of a team funded by the International Space Science Institute (ISSI). Therefore, a certain focus will be on the chemistry of methane and hydrocarbons.

2. Experiments on reactions involving methane in the interstellar medium

Methane has no permanent electric dipole moment because of its tetrahedral symmetry. Therefore, it cannot be studied via radiofrequency observations of its pure rotational transitions, the most general method to study interstellar molecules. Instead, it be traced by observing its vibrational transitions in the infrared region of the electromagnetic spectrum (e.g. Knez et al. 2009). Interstellar excitation of vibrational levels of molecules like methane usually requires a strong background source that emits in the infrared, such as a very young or very old star. Therefore, observational studies of methane have been principally limited to the envelopes of dying stars such as IRC+10216 or CRL 618 (e.g. Cernicharo et al. 2001) and in dense molecular clouds with young, imbedded protostars (e.g. Boogert et al. 2004), including a few with protoplanetary disks (e.g. Gibb & Horne 2013). Detections of interstellar methane in fact are rather limited. Methane is clearly created from gas-phase, equilibrium chemistry in old stars, where the high densities and temperatures near the stellar photosphere promotes its formation (e.g. Charnley et al. 1995). Its origin in molecular clouds, on the other hand, may be through gas-phase reactions or on surface processes on dust grains, or both. Because the abundance and distribution of methane is not well-documented due to observational limitations, it is very important to understand its role and connection to other hydrocarbons that are more readily studied in the interstellar medium, such as C_3H or CCH, which have permanent electric dipole moments. Molecules such as these species are fairly universally found in interstellar sources, including planetary nebulae, diffuse clouds, and cold, dark clouds (e.g. Ziurys et al. 2015). They therefore serve as "proxy" molecules for methane, and relating their reaction pathways to those of methane, including photo-detachment of negative ions, is critical to obtain a complete picture of where CH_4 exits and its abundance.

2.1. Experimental studies into gas phase methane and hydrocarbon chemistry

Carbon-containing molecules, including methane and other hydrocarbons, play a decisive role in the chemistry of the interstellar medium (ISM) and the atmospheres of planets and their satellites. Also, hydrocarbons, including methane, are key components of the atmospheres of gaseous planets and their satellites (Sakai *et al.*, 2009), especially Titan, which has a methane cycle similar to the terrestrial water cycle and also contains hydrocarbon lakes on its surface. Many of the interstellar carbon-bearing molecules are thought to be formed by gas-phase processes. Such processes are important in prebiotic syntheses, as evidenced by the high degree of deuterium enrichment found in organic molecules extracted from meteorites, and also in the insoluble organic material (IOM) :e.g. Pizzarello et al. (2006). High D-enhancements cannot be accounted for easily by anything other than low temperature, gas-phase reactions (Millar 2005). Therefore, it is important to understand gas-phase reactions in the ISM.

Due to the low temperatures prevalent in the interstellar medium, neutral-neutral reactions between closed shell molecules are highly unlikely, since these processes usually have an activation energy barrier, which usually cannot be surmounted under interstellar conditions. Radical- and ion-induced reactions and processes on grain surfaces have to fill the gap. Furthermore, the low particle density in interstellar objects prevents three-body reactions. Nevertheless, a rich carbon chemistry has been detected in a multitude of interstellar objects like dark clouds and star-forming regions. The main pathways in this chemistry can be grouped under the following categories: (1) ion induced reactions, (2) radical- and atom-induced reactions, (3) photoprocesses (4) ion-electron and (5) ion-ion reactions. Examples are as follows:

Ion-neutral reactions

Radiative association: $CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$ (i)
Proton transfer: $CH_5^+ + CO \rightarrow CH_4 + HCO^+$ (ii)
Neutral transfer: $H_2 + CH^+ \rightarrow CH_2^+ + H$ (iii)

Radical- and atom-induced reactions

Neutral-neutral processes: $C + C_2H_2 \rightarrow C_3H + H$ (iv)

Photon-induced processes

Photoionisation: $CH_4 + h\nu \rightarrow CH_4^+ + e^-$ (v)
Photodetachment: $C_4H^- + h\nu \rightarrow C_4H + e^-$ (vi)

Ion-electron reactions:

Dissociative recombination: $CH_5^+ + e^- \rightarrow CH_4 + H$ (vii)

Ion-electron reactions:

Mutual neutralisation $H^+ + H^- \rightarrow H + H$ (viii)

Different reaction pathways including some of the above-mentioned processes have been postulated to form methane, hydrocarbons, and other C-bearing molecules. In the case of the methane, a generally accepted and unambiguous formation pathway is still missing. To identify feasible gas-phase pathways to form molecules in the ISM, knowledge of the rate constants and product branching ratios leading to these species is vital. The prediction of these parameters by theoretical calculations has been proven difficult for many reactions, especially dissociative recombination (Kokoouline *et al.*, 2011), and experimental investigation of interstellar reactions faces severe challenges. Ideally, experiments should be carried out under conditions (pressure, temperature, excitation state of the reactants) similar to those encountered in the ISM. In many experimental devices low pressures in the range of 10^{-11} mbar can be achieved, which are, however, still several orders of magnitude higher than those encountered in interstellar environments. Nevertheless, for most gas-phase studies it is crucial to exclude three-body processes, which is accomplished under these pressures (Geppert and Larsson, 2013). Matching the low temperatures in the ISM can be a bit more of an issue. Not only are many devices capable of investigating interstellar hydrocarbon reactions fairly large and thus difficult to cool efficiently. Nevertheless, cooled storage rings have recently been constructed in Heidelberg (von Hahn *et al.*, 2016; Zaifman *et al.*, 2005) and Stockholm (Schmidt *et al.*, 2013). Another issue is the "freeze-out" of reactants on the inner surfaces of the experimental apparatus at very low temperatures. Also, radical and ionic reactants are often produced in discharge devices. This creates species often in highly excited states. In a high vacuum, deactivation of these states can only happen by photon emission, and lifetimes for these decay processes might be high. In some set-ups like ion traps cooling by cold buffer gases before the experiment has been employed successfully (Gerlich and Borodi, 2009). Also supersonic expansions have been used to cool reactants (McCall *et al.*, 2004).

Also, many of the reactants in interstellar chemistry are difficult to produce without by-products. For ions, mass spectrometers and deflection magnetic fields can be used to separate the desired reactant from contaminants (which only works if they have different masses, so different isomers and isobars cannot be separated). In case of radicals, production of pure, cool reactants can be difficult. However, hydrogen atoms generated by discharges can be equilibrated to cool temperatures by flowing through cold accommodator nozzles (Gerlich *et al.*, 2012). We will now briefly discuss the different experimental methods to investigate the above-mentioned processes.

For investigations of ion-neutral reactions, selected ion flow tubes (SIFT) and ion traps have been proven successful. A scheme of the selected ion flow tube is depicted in Fig. 1.

FIG. 1. Scheme of a selected ion flow tube apparatus.

In this technique the ions produced in the source are mass-selected by a quadrupole mass filter. The carrier gas entered into the tube moves the ions to the reaction zone, in which the reaction gases are added. Product ions formed by the ion−neutral reactions are mass selected and detected by a channeltron. A multitude of ion-neutral reactions involving hydrocarbons has been studied with SIFT (Anicich *et al.*, 2004).

Also radiofrequency ion traps like the 22-pole ion trap developed by Gerlich and co-workers (Gerlich, 2003) are used to investigate ion-neutral reactions. In such devices the ions, which have previously been mass selected, can be cylindrically trapped by an electrical field changing on a time scale comparable to radiofrequencies. The axial trapping is performed by charged end caps. During the trapping time, ions can be cooled by cold buffer gases, whereupon the reactant gas is added to the ion trap. After a certain reaction time the ions are axially ejected from the trap by an electrical field. The decay of the reactant ion and the build-up of product ions can be followed through detection of these ions after different reaction times. For example, the rate constant of the reaction

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu. \tag{9}$$

was measured in an ion trap as 6×10^{-15} cm^3 s^{-1} at 80 K by Gerlich and Kaefer (1989). The obtained value is almost 50 times the value predicted by previous theoretical calculations (Bates, 1987). Nevertheless, due to the high amount of H_2 present in dark clouds, the process is still feasible.

Ion traps can also be employed to investigate photodetachment of anions. The absolute cross sections of the anions of the photodetachment of the interstellar hydrocarbon anions C_4H^- and C_6H^- as well as C_3N^- and C_5N^- could recently be determined in a study using ion traps (Best et al., 2011, Kumar *et al.* 2013). Such photodetachment reactions, which, in the case of C_4H^- and C_6H^-, lead to neutral hydrocarbons that can further be involved in the hydrocarbon chemistry of the interstellar medium and planetary atmospheres. These processes can play a pivotal role in photon-dominated regions of dark clouds, from which the abundances of molecular anions can be inferred. Even in the inner parts of dark clouds in which UV photons cannot penetrate, UV photodetachment can still constitute a route of destruction of anions because secondary electrons produced by cosmic rays can excite molecules to high Rydberg states, which emit UV radiation upon decay. Furthermore, photodetachment of negative ions is one of the major destruction mechanisms in circumstellar envelopes. Model calculations of the circumstellar envelope IRC+10216, predicted, that in regions where anions display their peak abundance, photodetachment constitutes as the most efficient destruction mechanism of these species (Kumar *et al.* 2013).

Furthermore, photodetachment is an important destruction process of anions in the upper layers of Titan's ionosphere (Vuitton et al. 2009).

FIG. 2. Schematics of a flowing afterglow apparatus

Ion–electron reactions can be studied with flowing afterglow devices, merged beams, and storage rings. In the ISM, ion–electron reactions of molecules are almost restricted to exclusively dissociative recombination, since possibly competing processes are either too slow (radiative recombination) or highly endoergic (e.g. dissociative ionization). Many dissociative recombination reactions have been studied with the flowing afterglow technique (Schmeltekopf and Broida, 1963; Ferguson et al., 1964) , which is a further development of the earlier stationary afterglow method and has the advantage that the environments of ion production and reaction are spatially separated. In a flowing afterglow apparatus (see Fig. 2) usually He^+ ions are created by a microwave discharge. Downstream in the gas flow the reactant ions are produced through reactions of appropriate precursor molecules with He^+, sometimes via a sequence of several reactions. Further on the reactive gas is added and the decay of the probe ions can be followed by a mass spectrometer, since the distance between the reagent inlet and the mass spectrometer can be varied. A movable Langmuir probe can serve to follow the decay of the electrons. This Flowing Afterglow Langmuir probe (FALP) technique (Smith *et al.*, 1984) is used to determine the rate and, in some cases, also the products of dissociative recombination.

Furthermore, magnetic storage rings have been used to determine the rates and branching ratios of dissociative recombination reactions. As an example the CRYRING storage ring which was located at Stockholm University is depicted in Fig. 3. In a storage ring, ions are usually produced in a hollow cathode discharge or a tandem accelerator. After being mass selected by a bending magnet, they are injected into the ring. Thereafter, they are stored for several seconds to allow for radiative cooling. In a segment of the ring called the electron cooler, they are the merged with a cold electron beam at low relative kinetic energies down to several meV or even lower. The neutral fragments leave the ring tangentially and can then be detected. The employment of the grid method (Larsson and Thomas, 2001) or energy-sensitive multi-strip surface-barrier (EMU) detectors (Buhr *et al.*, 2010) allows determination of the branching fractions between different reaction pathways. As mentioned, dissociative recombination reactions are highly exoergic and can usually show 2 or more different energetically feasible reaction channels. Also, break-up of the ion into 3 fragments upon dissociative recombination is much more common than in predicted by previous theoretical studies (Bates, 1986). This is, for instance, the case in the dissociative recombination of protonated methane:

$$CH_5^+ + e^- \rightarrow CH_4 + H \tag{10a}$$

$$\rightarrow CH_3 + 2H \tag{10b}$$

$$\rightarrow CH_3 + H_2 \tag{10c}$$

$$\rightarrow CH_3 + H_2 + H \tag{10d}$$

in which Reaction (10a) represents only 5 % of all recombination processes and reaction 10b is the major pathway (Semaniak *et al.*, 1998). This fact has raised questions about the feasibility of the former process as the final step in the formation of methane in the ISM (Viti *et al.*, 2000). Hydrogenation of carbon by H atoms on interstellar grain surfaces has been discussed as alternative mechanism (Bar-Nun *et al.*, 1980).

In some cases there have been differences between rate constants measured by flowing afterglows and in storage rings. For the dissociative recombination, the storage ring measurements (Smith *et al.*, 1984) yielded a rate constant of $2.8\ (T/300)^{-0.52} \times 10^{-7}\ \text{cm}^3\ \text{s}^{-1}$ whereas afterglow experiments reported considerable higher values, amounting up to $1.1 \times 10^{-6}\ \text{cm}^3\ \text{s}^{-1}$ at 300 K (Adams *et al.*, 1984). This discrepancy can be caused by different reasons. In afterglow studies, where usually higher pressures pertain, three-body reactions involving the buffer gas or another reactant molecule or atom must be taken into account. Also, highly excited intermediate neutral molecules formed by the attachment of the electron or highly excited neutral fragments can be cooled by collisions with buffer gases and consequently follow a different reaction pathway. On the other hand, ions in excited states that show different behaviour in dissociative recombination from those in the ground states could be present in the storage ring experiments.

FIG. 3. The CRYRING storage ring

Crossed-beam experiments have proven a powerful tool for investigating neutral-neutral reactions. In these devices, two supersonic beams (one containing the atom or radical and one the other reactant) are crossed. Often the intersection angle can be scanned in these devices enabling continuous variation of the relative kinetic energy of the reactants. Detection of the products can be accomplished with laser-induced fluorescence and mass spectrometry. The reaction of carbon at very low translational energy of the reaction of carbon atoms with unsaturated hydrocarbons, e.g.,

$$C_2H_4 + C \rightarrow C_3H_3 + H \qquad (11)$$

which could be an important step in the build-up of larger hydrocarbons could be measured at relative translational energies down to 0.5 kJ/mol (Geppert *et al.*, 2000). With so-called "soft ionization" of product species by electrons with low energies and subsequent detection of the ions by mass spectrometry even different products of the atom-neutral reaction could be identified (Balucani *et al.*, 2006).

For determining the rate constant of atom-neutral reactions the CRESU (Cinetique des Reactions en Ecoulement Supersonique Uniforme) apparatus has been employed with great success for studying hydrocarbon reactions at ISM temperatures (Canosa *et al.*, 1997). In the CRESU these cold temperatures are achieved by expanding the reactants and the radical precursors in buffer gas through a supersonic flow through a convergent-divergent Laval nozzle, whereby the buffer gas makes up the vast majority (~99 %) of the gas mixture. Reactant atoms and radicals can then be produced from the precursor through irradiation of a coaxial laser.

FIG. 4. Schematic of the CRESU apparatus.

The decay of the reactant atom (e.g. $C(^3P)$) can then be followed by laser-induced fluorescence since the distance between the movable reservoir and the detection zone can be continuously altered and the velocity of the gas flow is well defined. Pseudo-first order conditions (excess of the neutral reactant gases, e.g. acetylene relative to the reacting atoms or radicals) are usually employed, which enables measurement of the rate constants. Very low temperatures (down to 15 K) can be routinely achieved in the CRESU device. Also the supersonic flow acts as a wall-free reaction vessel excluding problems arising from reaction on the chamber walls, which can be a problem in flow tubes. As can be seen in Fig. 4., the CRESU device can also be used for ion-neutral reactions (Rowe *et al.*, 1984).

Unfortunately there is not very much data available about cation-anion reactions (e. g. mutual neutralization processes), since these are very demanding to study experimentally.

Investigations of ion-ion reactions require production and mixing of two ions under very controlled conditions (Adams *et al.*, 2003). Merged beams (Moseley *et al.*, 1975) and flowing afterglow (Smith and Adams, 1983) have been employed to study these processes. The construction of the DESIREE double storage ring, will allow investigations of mutual neutralization reactions of interstellar anions (C_4H^-, C_6H^- and C_4H^-) with cations under interstellar conditions, since a very high vacuum and the cooling of the whole ring to temperatures less that 10 K are envisaged for this device (Schmidt *et al.*, 2013).

It would be beyond the scope of this review article to discuss the importance of all gas-phase neutral and ion reactions. Regarding the latter processes, the reader is referred to the review by Larsson et al (2012). However, it can be seen from this summary that a multitude of experimental devices have been used to study gas-phase reactions in the ISM. All these approaches have their advantages and shortcomings, so disagreements in reaction rates and product branching ratios obtained by different methods still exist. However, for many important interstellar chemical gas phase processes, still very little experimental data exists. This is unfortunate, since model calculations need reliable kinetic parameters of these reactions as input data. New devices in the future will hopefully amend this lack of information.

A critical collection of data on different astrophysically relevant gas-phase reactions is provided by the KIDA (Kinetic Database for Astrochemistry) database (Wakelam et al. 2015). It can be accessed via the web under http://kida.obs.u-bordeaux1.fr/.

2.2 Experimental investigations of reactions on the surface of interstellar dust grains

It is generally recognized that surface processes on dust grains play an important role in the synthesis of both hydrogen molecules and of water and organic molecules. Although sequences of gas-phase chemical reactions can lead to the formation of a multitude of molecules, in many cases they are inefficient in interstellar environments because of the presence of rate-limiting processes along the reaction chain. For example, in the gas phase, H_2 formation through recombination (i.e. radiative association) of two hydrogen atoms in the ground state is forbidden. Instead, H_2 formation requires associative detachment, $H^- + H \rightarrow H_2 + e^-$. Formation of H^- by radiative electron attachment is slow and acts as the rate-limiting process, thus the latter process was only dominant in the late stages of the primeval universe. Grain-surface processes have several advantages compared with gas-phase reactions: (1) energetic processes like photolysis and ion bombardment of grain ice mantles, which contain many chemical species, can efficiently produce complex molecules; (2) even reactions characterized by small cross sections, which rarely occur through single collisions in the gas phase, may proceed because reactants stay nearby and interact for a long time on the grain surface at very low temperatures; and (3) the surface acts as an absorber of excess energy of reaction and thus recombination—such as H_2 formation and addition reactions—occurs efficiently without dissociation. Formation of hydrogenated molecules, e.g. organic molecules, particularly benefits from these advantages on grain surfaces for a number of reasons. First, adsorbates can easily react with hydrogen produced by photolysis or ion bombardment of H_2O, which is the major component of ice mantles. Second, with reference to advantage (2), hydrogen addition reactions, even if characterized by moderate activation energies, can be facilitated through quantum tunneling at very low temperatures, where thermally activated reactions are highly suppressed. Quantum tunneling becomes feasible when the de Broglie wavelength of particles is comparable to the width of the activation barrier. In other words, tunneling is particularly effective for reactions involving light atoms, such as hydrogen, at very low temperatures because the wavelength is proportional to $(mT)^{-1/2}$. In addition, radical–radical recombination and tunneling reactions do not require any external energy input, like photons and ions, to proceed. This is particularly crucial for molecular synthesis in dense clouds, where radiation fields are very weak.

Among all hydrogenated molecules ever found in the actual ice mantles of interstellar grains, relatively simple molecules such as H_2O, CH_4, NH_3, H_2CO, and CH_3OH can be formed by simple H-atom addition to more primordial species on the grain surfaces. In fact, in recent years many studies have been published about the formation of these molecules through grain-surface reactions of H atoms (for a review, see Watanabe and Kouchi 2008). The formation processes of these molecules compete with each other. For example, methane can be produced by successive hydrogenation of C atom while methanol results from hydriogenation of CO on grains. The abundance of the simple hydrogenated molecules are strongly related with hydrogenation reaction rates and accretion rates of parent species: C, CO, and N. In fact, it was proposed that the formation of abundant carbon chains observed towards warm protostellar cores can be triggered by sublimation of CH_4 molecules from dust grains, where accretion of C atoms on dust exceed that of CO (Sakai and Yamamoto, Chem. Rev. 113, 8981 (2013)). In contrast, in star forming regions where the carbon chain molecules are deficient, the accretion rate of CO would be larger and lead to

H_2CO and CH_3OH. It is therefore useful to overview the formation processes of not only CH_4 but also other competing molecules. In this section, the formation mechanisms of such hydrogenated molecules on cold grain surfaces are briefly reviewed, with a focus on experimental results.

CH_4 and NH_3

Methane has been observed in both the gas (Boogert *et al.* 1998) and solid (Boogert *et al.* 1996) phase toward high-mass and low-mass protostars. In addition to gas-phase formation, surface reactions are required to explain both the presence of CH_4 in polar ice and its low gas/solid abundance ratio. Similarly, both solid and gaseous NH_3 have been found at higher abundances than CH_4 in a number of different objects. Although a series of ion–molecule reactions have been proposed to form NH_3 from N atoms or N^+ ions, grain-surface reactions are often considered as a major formation route. The most plausible route for CH_4 and NH_3 formation on grain surfaces is through successive H-atom addition (hydrogenation) to C and N atoms ($C \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4$ and $N \rightarrow NH \rightarrow NH_2 \rightarrow NH_3$), respectively. The number of experiments focusing on hydrogenation of C and N atoms on surfaces is still rather limited because of technical difficulties related to C- and N-atom preparation. Hiraoka *et al.* sprayed atomic hydrogen onto C (Hiraoka *et al.* 1998) and N (Hiraoka *et al.* 1995) atoms in CO and N_2 matrices, respectively, in the temperature range of 10–30 K. They subsequently detected CH_4 and NH_3 using temperature-programmed desorption (TPD) methods, although it was not clear whether CH_4 and NH_3 were formed at 10 K or during the subsequent heating. Recently, Hidaka *et al.* (2011) observed NH_3 formation in situ upon the exposure of N atoms in an N_2 solid to H atoms at 10 K using Fourier-transform infrared reflection-absorption measurements. Unfortunately, the experimental conditions of these studies were not very relevant for realistic grain surfaces. Use of ice, silicate, or carbonaceous material substrates is desirable to appropriately simulate grain-surface processes. Nevertheless, it is reasonable to infer that the successive hydrogenation of C and N atoms proceeds on the grains because every step is a radical–radical barrierless or low-barrier reaction, assuming a physisorption system. The formation rate of the radical–radical hydrogenation reaction on grain surfaces at very low temperatures should be limited by the surface diffusion of atomic hydrogen or the accretion rates of C or N atoms. Surface diffusion of atomic hydrogen was recently investigated experimentally on amorphous solid water (ASW) at 10 K. From direct measurements of H atoms on ASW, it was found that most adsorption sites on ASW are sufficiently shallow for H atoms to thermally migrate from site to site, even at 10 K (Watanabe *et al.* 2010; Hama *et al.* 2012). Therefore, once H, C, and N atoms land on the grain surface, the diffusion rate of H atoms would not suppress the formation of CH_4 and NH_3. Instead, exothermic abstraction reactions with H atoms from intermediate radicals, e.g. NH + H $\rightarrow$ N + H_2 and CH + H $\rightarrow$ C + H_2, may compete with addition reactions and slow down the formation of CH_4 and NH_3. Experiments on this kind of abstraction reaction are highly desirable.

H_2CO and CH_3OH

Since solid H_2CO and CH_3OH have been found abundantly in ice mantles, their formation mechanisms have been thoroughly investigated. Theoretical studies first suggested that these molecules are formed through successive hydrogenation of CO on grains, i.e., CO $\rightarrow$ HCO $\rightarrow$ H_2CO $\rightarrow$ CH_3O (or CH_2OH) $\rightarrow$ CH_3OH (e.g. Tielens and Whittet 1997). There is a critical difference between the formation of H_2CO and CH_3OH on the one hand and CH_4 and NH_3 on the other. The successive hydrogenation of CO, leading to H_2CO and CH_3OH, includes radical-formation processes, CO + H $\rightarrow$ HCO and H_2CO + H $\rightarrow$ CH_3O, which have significant activation barriers in the approximate energy in temperature range of 2000–3000 K (Woon 2002). Conversely, successive hydrogenation of C and N atoms consists of radical–radical barrierless or low-barrier reactions only. At very low grain temperatures, H_2CO and CH_3OH formation through thermally activated hydrogenation is highly inhibited and thus requires quantum-tunneling reactions. Because the CO reactant can be readily prepared on a cold substrate in laboratory settings, CO hydrogenation has been targeted by many experimentalists. Since the first attempt where H_2CO formation was observed using the TPD method (Hiraoka *et al.* 1994), a number of improved experiments have been performed (e.g. Watanabe and Kouchi 2002; Watanabe *et al.* 2004; Fuchs *et al.* 2009). Watanabe and Kouchi (2002) demonstrated experimentally for the first time that H_2CO and CH_3OH are both produced at 10 K by exposure of H_2O–CO amorphous ice to cold H atoms. In subsequent experiments, they elucidated the effects of various parameters—such as surface temperature and composition (Watanabe *et al.* 2004, 2006)—on hydrogenation of CO.

The same reaction system has been investigated by two other groups, and essentially the same results were obtained (Fuchs *et al*. 2009; Pirim and Krim 2011). The main findings of these experiments were the following: H_2CO and CH_3OH are efficiently formed by CO hydrogenation through quantum tunneling on dust-grain analogues even at 10 K. Upon exposure of CO on ASW to H atoms with fluences equivalent to those in molecular clouds over 10^5–10^6 yr, yields of H_2CO and CH_3OH reproduced abundances of the solids observed in ice mantles (Watanabe *et al*. 2003). To evaluate more quantitatively whether this hydrogenation process works in realistic interstellar conditions, competing reactions should be considered. Among reactions involving hydrogen atoms on grain surfaces, H_2 formation through H–H recombination is the most important process. The CO hydrogenation rate is proportional to the surface number density of H atoms, while the recombination rate is proportional to its square. In laboratory experiments, H_2 formation must be enhanced because of the expected higher H-atom number density. This can be understood when we realize that the H-atom fluxes used are several orders of magnitude larger than those in interstellar environments. As a result, H_2CO and CH_3OH formation would be rather more efficient in interstellar clouds than in the experiments. The impact of the surface composition and temperature on CO hydrogenation is also an astrochemically important factor. The CO hydrogenation rate on ASW gradually decreases as the temperature increases to 15 K and drops drastically at temperatures greater than 20 K (Watanabe *et al.* 2004). This temperature dependence can be attributed to the significantly reduced residence time of H atoms (i.e., to the number density of H atoms) on the ASW surface at those temperatures. That is, the desorption rate of H atoms exceeds the tunneling-reaction rate with increasing temperature. Experimental results indicate that CO hydrogenation by “nonenergetic” H atoms would be inefficient on grains at temperatures in excess of 20 K. Note that translationally energetic H atoms produced by photolysis or ion bombardment of molecules like H_2O can still react with CO even at temperatures greater than 20 K within ice mantles, because such energetic atoms can overcome the reaction’s activation barrier immediately and, therefore, tunneling which requires significant residence time on the surface is not necessary. The role of solid H_2O, the main component of ice mantles, in the context of CO hydrogenation has been highlighted experimentally by comparison with results related to the hydrogenation of pure solid CO. The hydrogenation rate of CO on ASW is almost equivalent to that of pure solid CO around 10 K for the same H-atom flux. However, at temperatures above 12 K, the difference in hydrogenation rates between both systems becomes considerable. The CO hydrogenation rate on pure solid CO is approximately three orders of magnitude smaller than that on ASW at 15 K (Watanabe and Kouchi 2008). Since the CO hydrogenation rate is proportional to both the residence time of H atoms on the surface and the tunneling transmission rate for the reaction's potential barrier, the ASW surface should enhance either or both compared with pure solid CO surfaces. However, it is unlikely that the existence of H_2O molecules substantially modifies the shape of the potential barrier for CO + H $\rightarrow$ HCO, which governs the tunneling transmission rate, because interactions of both H and CO with H_2O are of van der Waals type. Therefore, enhancement of hydrogenation on ASW would be attributed to an increase in the residence time, i.e., an increase of the surface number density of H atoms. It is plausible that a surface composed of molecules with a larger dipole moment produces a higher physisorption energy for H atoms. The dipole moment of H_2O is approximately 20 times larger than that of CO, so that H atoms would stay longer on ASW than on pure solid CO. The effect of the ASW surface on the temperature dependence of the tunneling reactivity varies with the reactions in the physisorption system. Fast reactions, which do not need long interaction times with H atoms, should be less affected by the ASW.

Interstellar formaldehyde (Loinard *et al.* 2000) and methanol (Parise *et al.*, 2006) are well-known highly deuterated species. The high deuterium enrichment in these molecules cannot be explained easily by invoking pure gas-phase chemistry. It is reasonable to consider that surface reactions contribute significantly to the formation of deuterated formaldehyde and methanol, as they do to the formation of normal H_2CO and CH_3OH. Theoretical models (Charnley *et al.*, 1997) have proposed successive additions of H and D atoms to CO on grain surfaces as a route for the formation of deuterated formaldehyde and methanol. Hidaka *et al.* (2007) first quantitatively evaluated deuteration of CO on ASW and found that deuterium addition, CO + D $\rightarrow$ DCO, is slower by approximately one order of magnitude than hydrogen addition, and that simple addition of D atoms to CO is inefficient. When considering the isotope effect of the tunneling reaction, this is readily understandable. Tunneling reactions are very sensitive to the tunneling mass and become considerably slower for heavier isotope masses. Nagaoka *et al.* (2005) first revealed experimentally that H–D substitution reactions occur on low-temperature surfaces following cold (30–100 K) D-atom exposure of solid CH_3OH, i.e., $CH_3OH \rightarrow CH_2DOH \rightarrow CHD_2OH \rightarrow CD_3OH$, probably via a sequence of H abstraction and D addition. The backward processes leading to a reduction in the number of D atoms in molecules (e.g. $CH_2DOH \rightarrow CH_3OH$) was not observed upon exposure to H atoms. Isotopologues containing D in the hydroxyl group (Me–OD) have not been observed. Similarly, deuterated formaldehyde is produced very efficiently by H–D substitution of normal formaldehyde (Hidaka *et al.*, 2009). These results have first indicated that H-D substitution reactions on the grain surfaces work for deuterium enrichment of formaldehyde and methanol. The non-detection of Me–OD in the experiments is consistent with the low abundances of Me–OD molecules observed. Based on these experimental results, Taquet *et al.* (2012) recently proposed a model that showed that D- and H-atom abstraction and substitution reactions are crucial in grain-surface chemistry and should be incorporated in models.

H_2O

H_2O is the most abundant component observed in ice mantles. Its abundance cannot be explained merely by gas-phase synthesis (e.g. Hasegawa *et al.*, 1992). The formation of solid H_2O has been intensively studied experimentally in recent years. The simplest route of H_2O formation is by successive addition of H atoms to an oxygen atom ($O \rightarrow OH \rightarrow H_2O$). Hiraoka *et al.* (1998) and Dulieu *et al.* (2010) reported that this formation route works on cryogenic surfaces. In their experiments, nondissociated O_2 molecules and O_3, which result from the surface reaction $O + O_2$, coexist on the sample surfaces. Since these molecules can be additional sources for H_2O, as described below, it is not easy to determine the formation efficiency of H_2O through successive hydrogenation of O atoms alone under such experimental conditions. Nevertheless, it would be safe to consider that successive hydrogenation of O atoms proceeds efficiently on grain surfaces, because every step is radical–radical reaction. A theoretical model has predicted that successive H-atom addition to O_2 molecules ($O_2 \rightarrow HO_2 \rightarrow H_2O_2 \rightarrow H_2O + OH$), combined with the reaction $OH + H_2 \rightarrow H_2O + H$, considerably contributes to H_2O formation in dense molecular clouds (Cuppen and Herbst 2007). The final step of the former process, $H_2O_2 + H \rightarrow H_2O + OH$, and the latter reaction, $OH + H_2 \rightarrow H_2O + H$, have significant barriers and thus rarely occur at grain temperatures through thermally activated reactions. Miyauchi *et al.* (2008) demonstrated experimentally that successive hydrogenation of O_2, leading to the formation of H_2O, occurs efficiently even at 10 K through quantum tunneling. Subsequently, Ioppolo *et al.* (2008) also confirmed the efficacy of this process. Recently, a large isotope effect on the reaction $H_2O_2 + H \rightarrow$

H_2O + OH has been reported as a feature of the tunneling reaction (Oba *et al.*, 2014). For the reaction of OH with H_2, Oba *et al.* (2012) presented the first experimental evidence of solid H_2O formation through the tunneling reaction of OH (in its electronic and vibrational ground states) + H_2 at 10 K. Using isotopologues such as OD and D_2, they found that a significant isotope effect results from differences in the effective mass of each reaction. H_2O can also be formed through hydrogenation of O_3 (Mokrane *et al.* 2009; Romanzin *et al.* 2011). However, O_3 has not been observed in the interstellar medium, in neither gas nor solid phases. In fact, Taquet *et al.* (2013) predicted that O_3 is a minor product on grain surfaces.

2.3 Experiments simulating reactions in ice mantles of interstellar grains

Reactions of CH_4 / CH_3OH in simulated ice mantles of interstellar grains

Solid CH_4 has been observed towards low- and high- mass young stellar objects (Lacy *et al.*, 1991; Boogert *et al.*, 1996, 1997; Gibb *et al.*, 2004; Oberg *et al.*, 2008). Its abundance with respect to solid water varies in the range 2-10% (Boogert *et al.*, 1997; Oberg *et al.*, 2008). CH_4 is believed to be formed on grains either by hydrogenation (Aikawa *et al.*, 2005; Oberg *et al.*, 2008) of accreted C-atoms or by energetic processing of CH_3OH-rich ices (Boogert *et al.*, 1996; Baratta *et al.*, 2002; Garozzo *et al.*, 2011). In fact it is widely accepted that icy grain mantles are continuously processed by low-energy cosmic rays and UV photons (Jenniskens *et al.*, 1993; Shen *et al.*, 2004). Recently, Shen *et al.* (2004) have estimated the energy deposition onto water-ice grain mantles by cosmic rays and by UV photons in dense molecular clouds. They have found that depending on the assumed cosmic-ray spectrum at low energy, after 10^7 years the dose deposited by UV photons varies in the range 100-10 eV/molecule and the dose deposited by cosmic rays varies in the range 10-1 eV/molecule.

In the past 35 years several experiments have been performed to study the effect of ion bombardment and UV photolysis on the chemical composition of icy samples. In fact several laboratories worldwide are involved in this kind of study (e.g. Sandford *et al.,* 1988; Palumbo and Strazzulla 1993; Gerakines *et al.,* 1996; Cottin *et al.,* 2003; Bennett *et al.,* 2006; Oberg *et al.,* 2009; Fulvio *et al.*, 2009; Boduch *et al.,* 2012; Modica *et al.,* 2014; Munoz Caro *et al.*, 2014). Icy samples are prepared in a high vacuum (HV; P $\sim 10^{-7}$ mbar) chamber or ultra high vacuum (UHV; P $\sim 10^{-9}$ mbar) chamber. An infrared-transparent substrate (e.g. crystalline silicon or KBr) is placed in thermal contact with a cryostat and is cooled down to 10-20 K. Gases are admitted into the vacuum chamber in order to accrete a thin ice film (0.1-10 μm). Icy samples can be processed by fast ions (E= keV-MeV) or UV photons (obtained by a discharge lamp or synchrotron radiation). The ice samples can be analyzed before and after processing by infrared transmission spectroscopy or Refection Absorption IR (RAIR) spectroscopy.

Laboratory experiments have shown that CH_4 is easily destroyed by ion bombardment or UV photolysis (e.g. Gerakines *et al.*, 1996; Baratta *et al.*, 2002). As an example Figure 5 shows the column density of CH_4 after ion bombardment of pure CH_4 and a mixture H_2O: CH_4=4:1 at 12 K. Column density values are plotted versus dose (given in eV/16u). The dose is obtained from the knowledge of the ion fluence impinging on the sample (ions cm^{-2}) measured during the experiment and the stopping power (eV cm^2 $molecule^{-1}$) obtained using SRIM 2008 code (Ziegler *et al.*, 2008). As suggested by Strazzulla and Johnson (1991), the dose given in units of eV per small molecule (16u) is a convenient way to characterize chemical changes and to compare the results obtained after processing of different samples. Experimental data reported in Fig. 5 are adapted from Baratta *et al*. (2002) and Garozzo *et al*. (2011). The column density is obtained from the CH_4 band at about 1300 cm^{-1} using a band strength value equal to 6.4×10^{-18} cm $molecule^{-1}$ (Mulas *et al*., 1998) after the transmission spectra are converted to optical depth scale. The column density of CH_4 at a given dose is divided by the value measured soon after deposition (i.e. before bombardment starts). We notice that the CH_4 column density ratio has values greater than 1 at low dose. As pointed out by Garozzo *et al*. (2011) this is due to the variation in the band strength value after ion bombardment as also observed for other bands in other molecules (e.g. Leto and Baratta, 2003; Loeffler *et al*., 2005).

FIG. 5. Normalized column density of CH_4 as a function of irradiation dose (eV/16u) after ion bombardment of pure CH_4 and a H_2O:CH_4=4:1 mixture at 12 K with 30 keV He^+.

After bombardment new absorption bands are observed in the infrared spectra which indicate the formation of additional volatile species such as ethane (C_2H_6), propane (C_3H_8), ethylene

(C_2H_4) and acetylene (C_2H_2). When CH_4 is mixed with H_2O and/or N_2 other and more complex species are formed (e.g. Moore and Hudson, 1998, 2003; Baratta *et al.*, 2002, 2003). In any case after further bombardment a refractory residue is formed as demonstrated by the appearance of the amorphous carbon feature in the Raman spectra (e.g. Ferini *et al.*, 2004; Palumbo *et al.*, 2004). Recently, Brant and Kaiser (2013) have studied the effects of electron irradiation of pure CH_4 by reflectron time-of-flight mass spectrometry and have found that high-molecular-weight hydrocarbons of up to C_{22}, among them alkanes, alkenes and alkynes, are formed; Paardekooper et al. (2014) and Bossa et al. (2015) have investigated the effect of UV photolysis on pure CH_4 ice at 20 K combining laser desorption and time-of-flight mass spectrometry showing the formation of large C-bearing species.

Observations have shown that in icy grain mantles the abundance of methanol (CH_3OH) with respect to H_2O along the line of sight of high-mass and low-mass young stellar objects spans over a large range: 1%-30% (Gibb *et al.*, 2004; Boogert *et al.*, 2008).

Recent laboratory experiments (e.g., Hiraoka *et al.*, 2002; Watanabe and Kouchi, 2002; Fuchs *et al.*, 2009) have shown that CH_3OH molecules efficiently form after hydrogenation of CO molecules in CO-rich and water-poor ices. Therefore it is reasonable to assume that CH_3OH-rich and water-poor ice mantles may exist along the line of sight of dense molecular clouds (e.g., Skinner *et al.*, 1992; Palumbo and Strazzulla, 1992; Cuppen *et al.*, 2011). When methanol is processed by energetic ions the column density of pristine methanol decreases and new bands appear in the infrared spectra indicating the formation of other, also complex, species (e.g. Palumbo *et al.*, 1999; Baratta *et al.*, 2002; Oberg *et al.*, 2009; Bennett *et al.*, 2007). Figure 6 (top panel) shows the normalized column density of methanol after ion bombardment at 16 K of pure CH_3OH and $CO:CH_3OH$ and $N_2:CH_3OH$ mixtures as a function of dose in eV/16u. Experimental data are adapted from Modica and Palumbo (2010) and Islam *et al.* (2014). The column density of methanol is obtained from the band at about 1030 cm^{-1} using the band strength value of 1.3×10^{-17} cm molecule^{-1} (Palumbo *et al.*, 1999). Figure 6 (bottom panel) shows the ratio between the column density of CH_4 formed after processing and the column density of CH_3OH at the same dose. We notice that this ratio is independent of the initial mixture within experimental uncertainties. Several other species are formed after ion bombardment of CH_3OH-rich mixtures such as carbon monoxide (CO), carbon dioxide (CO_2), formyl radical (HCO), formaldehyde (H_2CO), ethylene glycol

($C_2H_4(OH)_2$), methyl formate ($HCOOCH_3$), and glycolaldehyde ($HCOCH_2OH$) (e.g. Moore *et al.*, 1996; Palumbo *et al.*, 1999; Hudson and Moore, 2000; Modica and Palumbo. 2010).

FIG. 6. Top panel: Normalized column density of CH_3OH as a function of irradiation dose (eV/16u) after ion bombardment of pure CH_3OH and two mixtures, CO:CH_3OH and N_2:CH_3OH, at 16 K with 200 keV H^+. Bottom panel: Column density of CH_4 formed at 16 K after ion bombardment (200 keV H^+) of the same CH_3OH-rich ice mixtures divided by the column density of CH_3OH at the same dose.

The experimental results here described could be added to chemical models to understand the equilibrium value reached between CH_4 formation processes (i.e. hydrogenation of C-atoms and energetic processing of CH_3OH-rich ices) and the destruction processes induced by ion bombardment.

Ten different molecular species have been firmly identified in interstellar icy grain mantles. Among them CH_4 and CH_3OH have been detected towards both high-mass and low-mass young stellar object. From the data reported by Gibb *et al.* (2004) it is possible to estimate that towards high-mass young stellar objects the column density ratio CH_4/CH_3OH is on average less than one. On the other hand this ratio is higher, as high as two, towards low-mass young stellar objects (Oberg *et al.*, 2008; Boogert *et al.*, 2008). This difference could be ascribed to the different average ice temperature in the line of sight to high- and low-mass objects along with the different sublimation temperature of pristine CH_4 (about 30 K) and pristine CH_3OH (about 130 K; e.g. Collings *et al.*, 2004). However it is important to notice that volatile species can remain trapped in the refractory residue formed after ion bombardment and can be observed in the spectra taken at temperature higher than their sublimation temperature (e.g. Palumbo *et al.*, 1999; Sicilia *et al.*, 2012).

As shown in Fig. 6 (bottom panel), laboratory experiments show that the column density ratio CH_4/CH_3OH after ion bombardment of CH_3OH-rich ice is less than one in the dose range investigated (Palumbo et al., unpublished data). This suggests that ion bombardment of

CH_3OH-rich ices can be relevant but cannot be the only formation route to observed solid CH_4; hydrogenation of accreted carbon atoms is a relevant process too.

It is generally accepted that ice grain mantles are processed simultaneously by UV photons and low-energy cosmic rays. Several investigations on the comparison between the two processes have been carried out (e.g. Gerakines *et al.*, 2000, 2001; Cottin *et al.*, 2001; Baratta *et al.*, 2002; Munoz Caro *et al.*, 2014) and recently also investigations on the effects obtained after simultaneous processing have been performed (Islam *et al.*, 2014). Experimental results have shown that from a qualitative point of view, ion bombardment and UV photolysis generate similar changes in interstellar ice analogs. However, quantitative differences between the two processes have been observed.

Even if only ten species have been firmly identified it is generally accepted that other, more complex molecules are also present in icy grain mantles which cannot be detected in the solid phase by IR spectroscopy. These species are expected to enrich the gas phase composition after desorption of icy grain mantles (e.g. Palumbo *et al*., 2008: Modica and Palumbo, 2010) and could be incorporated in planetesimals and comets. To check the role of ion bombardment in the formation of complex species after ion bombardment of CH_4 and CH_3OH-rich ices we have compared the profile of the CH_4 band at about 1300 cm^{-1} observed towards dense molecular clouds with the profile we obtain in our laboratory spectra after ion bombardment. As an example Fig. 7 shows the comparison between the band profile observed with the ISO satellite towards the high-mass young stellar object NGC7538 IRS9 and the profile of the CH_4 band in different laboratory spectra. Figure 7 shows that a good comparison is obtained considering the contribution of two laboratory spectra namely a mixture $H_2O:CH_4$ after ion bombardment at low temperature and a CH_3OH-rich ice after ion bombardment at low temperature and warm up to 100-125 K. In each panel the red line is the best-fit to the observed data points obtained by a linear combination of two laboratory spectra. The thin lines are the laboratory spectra scaled by the coefficient given by the fit procedure. This result is consistent with the hypothesis that CH_4 formed after C hydrogenation is present on cold ice grain mantles along the line of sight and CH_4 formed after energetic processing of CH_3OH is also there. Here the temperature at which laboratory spectra are taken has to be regarded as the value at which the profile of the CH_4 band better reproduce the average profile along the line of sight due to icy grain mantles at different temperatures.

FIG. 7. Comparison between observed and laboratory spectra.

Many recent results support the experimental efforts (e.g. Allodi *et al*., 2013) to use more sensitive techniques to evidence the formation of complex molecules and/or fragments that could be of primary relevance for astrobiology also to understand which species should be searched for, by ground-based or space-born facilities, in protostellar environments, protoplanetary disks and in the atmospheres of extrasolar planets/moons that testify for the presence of a complex chemistry that could evolve toward a biosphere.

Formation of Complex Organic Compounds in Simulated Ice Mantles of Interstellar Grains

It was shown that interstellar dust particles in dense clouds are covered with ice mantles that are composed of water, carbon monoxide, carbon dioxide, methanol, methane and ammonia. The question is whether more complex organic compounds could be synthesized in the ice mantles. Greenberg proposed the following scenario: (1) Complex organic molecules were formed in ice mantles of interstellar dust particles (ISDs) in dense clouds: (2) The ISD complex molecules were altered by photochemical and thermal processes in diffused cloud, protosolar nebulae, etc., (3) The ISDs with organic molecules were aggregated to form comets (Greenberg and Li, 1997). It is not possible to observe complex organic compounds in the ice mantles; the only way to examine it is in laboratory simulation experiments.

The major energy for the reactions in the ice mantles seems to be cosmic rays and cosmic ray-induced ultraviolet light since stellar ultraviolet light cannot penetrate deeply into the dense clouds. In order to simulate possible reactions in ice mantles of interstellar dust particles, frozen mixtures of simulated interstellar media were irradiated with ultraviolet light or high energy protons.

Greenberg and coworkers performed pioneering laboratory simulation of photochemical formation of complex organic molecules from possible interstellar media. In their earlier works, a frozen mixture of H_2O, NH_3, CH_4 and/or CO was used as simulated ice mantles of ISDs. The starting gas mixtures were frozen onto aluminum substrates that had been cooled down to 12 K, and they were irradiated with vacuum UV light from a hydrogen lamp. The products were warmed up to room temperature, and the residues on the substrates were analyzed by GC/MS after trimethylsilyl (TMS)-delivatization. When a mixture of H_2O, NH_3 and CO was used, various molecules including glycine was identified in the products, while CH_4 was used in place of CO, no residues were observed (Briggs et al., 1992). Thus, several photolysis experiments after this work tended to use CO and/or CH_3OH rather than CH_4.

Muñoz Caro *et al.* (2002) irradiated a frozen mixture of H_2O, CO, CO_2, CH_3OH and NH_3 with vacuum UV light from a hydrogen lamp at 12 K. Bernstein et al. (2002) also used a frozen mixture of H_2O, CO, CH_3OH, HCN and NH_3 as a target of VUV irradiation at 15 K. Both teams detected a number of racemic amino acids after hydrolysis of the products.

In order to examine direct actions of cosmic ray particles, Kobayashi *et al.* irradiated a frozen mixture of H_2O, CH_4 (or CO) and NH_3 with 3 MeV protons from a van de Graaff accelerator, and confirmed the formation of amino acid precursors (compounds giving amino acids after hydrolysis) (Kobayashi *et al.*, 1995, Kasamatsu *et al.*, 1997a, b). In particles irradiation experiments, not only CO but also CH_4 gave amino acid precursors.

The results suggested that complex molecules including amino acid precursors could be formed in ice mantles of interstellar grains containing H_2O, CH_4 (or CO, CH_3OH) and NH_3 by the action of cosmic rays and cosmic ray-induced UV. In addition to these energies, thermal energies during warming the ice mantles from dense cloud environments to warmer environments would give additional effects in organic formation (Theule et al., 2013). These organic compounds could have been incorporated into small bodies such as asteroids and comets after the solar system was formed from the materials in dense clouds via solar nebula. Furthermore, it is of interest to study how interstellar complex organic compounds were altered to cometary and meteoritic complex organic compounds by photochemical, radiochemical and thermal / hydrothermal / hydrolytic alterations.

3. Experiments simulating submarine hydrothermal systems

Submarine hydrothermal vents were first discovered at the Galapagos spreading center in the late 1970s (Corliss *et al*., 1979). They have been universally found along boundaries of tectonic plates, and were regarded as favorable sites for chemical evolution toward the generation of life on Earth for the following reasons:

1) Reducing environments are favorable for abiotic synthesis of bioorganic compounds. Though it is controversial whether methane and other hydrocarbons were present in primitive Earth atmosphere, submarine hydrothermal systems are promising sites where methane is available even in the present Earth environments.

2) Thermal energies from magma could be available for the energy source of chemical evolution. Long-term heating at high temperature would destroy formed organic compounds, but organic compounds that were formed in hot environmentts could survive by thermal quenching when they erupted into cold seawater.

3) The interaction between hydrothermal fluid and rocks provided high concentration of various metal ions such as manganese, iron and zinc, which could work as catalysts for abiotic synthesis of organic compounds (Kobayashi and Ponnamperuma, 1985).

4) Phylogenetic trees built by molecular biological data suggested that the last universal common ancestor of terrestrial organisms (LUCA) was a thermophile: The birth place of terrestrial first life would have been a hot environment such as vicinity of submarine hydrothermal vents.

A wide variety of experiments have been performed to simulate possible reactions in submarine hydrothermal systems (SHSs) to study origins of methane in SHSs and formation and stability of organic compounds such as amino acids in SHSs. Holm and Andersson (2005) published eleven years ago in Astrobiology a review of hydrothermal organic chemistry experiments carried out up to that date.

3.1 Experiments simulating methane formation in hydrothermal systems

Few experiments have been designed to focus on the formation of methane solely in neither marine hydrothermal nor terrestrial geothermal systems. French (1962, 1970) was the first scientist to recognize hydrothermal systems as sites for abiotic synthesis of organic compounds. He suggested on the basis of experimental results that organic compounds are formed abiotically by processes like Fischer-Tropsch type (FTT) reactions between a high pressure gas phase and siderite or other carbonates plus iron-bearing minerals. He also proposed that suitable conditions could be attained by hydrothermal activity at moderate depth within Earth's crust, where the existence of a CH_4-rich phase would be favored by low fugacity of oxygen (fO_2). Simulations of organic geochemistry in hydrothermal system conditions following French have been entirely focused on more complex organic compounds than methane, particularly hydrocarbons and amino acids.

About the only hydrothermal simulation experiments that have been designed to focus on the formation of CH_4 (together with H_2) were performed by Neubeck *et al.* (2011, 2014). They conducted a series of low temperature (30, 50 and 70°C) experiments in which they tested the CH_4 and H_2 formation potential of olivine. Their results showed that not only was hydrogen formed from water because of partial oxidation of Fe(II) in the Fe-silicate fayalite of the olivine, but also that CH_4 was produced at these relatively low temperatures from CO_2 and HCO_3^-. Apparently, the presence of spinels like magnetite (formed by the oxidation of the fayalite) and chromite catalyze the formation of CH_4.

3.2 Formation of amino acids in SHSs-simulating environments

In order to examine possible formation of amino acids in submarine hydrothermal systems, Yanagawa and Kobayashi (1992) performed simulation experiments by using an autoclave. Modified hydrothermal vent media (MHVM) containing Fe^{2+} (2 mM), Mn^{2+} (0.6 mM), Zn^{2+} (0.1 mM), Ca^{2+} (0.1 mM), Cu^{2+} (20 mM), Ba^{2+} (0.1 mM) and NH_4^+ (50 mM) were prepared and the pH was adjusted to 3.6. MHVM in a Pyrex glass tube and a 1:1 mixture of methane and nitrogen (80 kg cm^{-2}) was introduced in the autoclave. They were heated at 325ºC for 1.5 – 12 h, and then was cooled down to room temperature. The resulting solution was subjected to amino acid analysis by HPLC and GC/MS after acid hydrolysis.

Amino acids such as glycine, alanine, aspartic acid and serine were detected in the hydrolysates, together with non-protein amino acids like α- and γ- aminobutyric acid, β-alanine and sarcosine. The amino acids detected by GC/MS with a chiral column were racemic mixtures. Procedural blank showed no amino acids. Thus it can be said that amino acid precursors were abiotically formed from methane-containing media in simulated submarine hydrothermal system environments (Yanagawa and Kobayashi, 1992).

A major challenge would be to quantify the abiotic formation of CH_4 and other organic compounds in hydrothermal environments on Earth today, on other celestial bodies, as well as on the early Earth.

4. Experiments on methane chemistry in planetary and satellite atmospheres

Among all the objects in the solar system, Titan and its methane-rich atmosphere provide a natural laboratory of chemical evolution. Thermal escape, and methane reactivity, including its direct photolysis, are responsible for a short lifetime of methane in Titan's atmosphere of about 20-30 Myr (Atreya 2006, Tucker and Johnson 2009, Krasnopolsky 2014). Methane chemistry is moreover strongly coupled with nitrogen, leading to heavy hydrocarbon and nitrogen-bearing organic molecules in the gas phase, and ultimately to solid organic aerosols settling down to Titan's surface. This complex chemistry is complementary probed by the Cassini-Huygens space mission and by laboratory experiments. The thickness of Titan's atmosphere leads to isolate two main reactive-layers in Titan's atmosphere: above the tropopause, driven by VUV photochemistry, and below the tropopause, driven by soft UV and interactions with the surface.

4.1 Reactions in the higher layers of Titan's atmosphere and ionosphere

One of the most surprising discoveries of the Cassini-Huygens mission to the Saturn system was the rich ion-neutral organic chemistry present in the thermosphere and ionosphere of Titan above 950 km altitude (Waite *et al.*, 2006). Three observation types characterize that discovery (see Fig. 8):

1) A strong correspondence between the neutral and ion species that were measured below 100 u by the Cassini Ion Neutral Mass Spectrometer (INMS) (see panel A).

2) An extension of the ion mass spectrum up to masses of >250 u observed the Cassini Plasma Spectrometer (CAPS) Ion Beam Spectrometer (IBS, Crary *et al*., 2009) (see panel B).

3) Large negative ions with masses greater than 5000 u seen by the CAPS Electron Spectrometer (ELS; panel C) that increase in complexity at altitudes below 1000 km (Coates *et al*., 2009).

Westlake *et al*. (2014) have demonstrated with correlation analysis that the molecular growth between ions and neutral below 200 u appears to take place in large part due to addition reactions of C_2 compounds (C_2H_2 and C_2H_4). Westlake *et al*. (2014), Waite *et al*. (2006) and Lavvas *et al*. (2013) argue that the processes of positive and negative ion growth of organic molecules can account for the bulk of the organic synthesis at Titan with largely agglomeration and condensation chemistry occurring below 800 km. This stands in strong contrast to the pre-Cassini-Huygens paradigm of organic synthesis in Titan's stratosphere.

4.2 Experiments simulating the higher layers of Titan's atmosphere

The triggering process for methane chemistry in Titan's higher atmosphere is its photolysis. Well characterized at Lyman-α (Romanzin, Bénilan et al. 2008, Gans, Boye-Peronne et al. 2011), the branching ratios among the photolytic products remain poorly documented out of this wavelength. No measurements exist between the branching ratios for CH_2 and CH_3 at wavelengths larger than Lyman-α (Gans, Peng et al. 2013). Titan's atmospheric models actually suffers from this lack of experimental data since the 130-140 nm wavelength range dominates methane photolysis in the stratosphere.

From Cassini observations we know that aerosols not only are bathed in a neutral and ion gas mixture that comprises Titan's ionosphere, but they also affect the content and charge balance of the gas phase itself (Lavvas et al. 2013). This feedback between ions, neutrals and solid aerosols is to date difficult to predict, but successfully approached in the laboratory by dusty-plasma experiments (Coll, Coscia et al. 1999, Imanaka, Khare et al. 2004, Szopa, Cernogora et al. 2006, Trainer, Pavlov et al. 2006, Cable, Hoerst et al. 2012). In this case partial ionization of the initial CH_4-N_2 gas mixture is created by a plasma discharge, similar to the combined effect of the magnetospheric electrons from Saturn and the VUV solar photons. Plasma experiments have provided support for the interpretation of Cassini-Huygens data. For instance specific investigation of the ion and neutral gas-phase content have been led in (Gautier, Carrasco et al. 2011), (Carrasco, Gautier et al. 2012) and (Horvath, Aranda-Gonzalvo et al. 2010), involving nitrile molecules, positive ions and negative ions respectively. Plasma experiments in the laboratory have also demonstrated that the addition of CO to the mixture (perhaps due to oxygen from Enceladus) can result in efficient oxygen incorporation in the aerosols (Fleury, Carrasco et al. 2014) and in amino acid formation (Hörst, Yelle et al. 2012)..

A new type of experiment mimicking Titan's ionospheric chemistry appears with the development of photoreactors coupled with VUV synchrotron beamlines (Imanaka and Smith 2010, Peng, Gautier et al. 2013). In the latter case, the dissociation and ionization processes occur through direct VUV photolysis of methane and molecular nitrogen. Neutral chemistry only, as in Titan's stratosphere, is also often simulated with experimental setups ensuring methane dissociation by softer VUV (such as Lyman-α wavelength) and UV sources (Tran, Ferris et al. 2003, Trainer, Jimenez et al. 2012).

Methane concentration varies significantly in the ionosphere of Titan according to the altitude (Waite Jr, Niemann et al. 2005, Hébrard, Dobrijevic et al. 2006) from 2 up to about 10%. This parameter is therefore often considered in laboratory simulations of Titan's ionosphere. A strong influence of the methane concentration on the aerosol production efficiency has been found in (Trainer, Pavlov et al. 2006, Sciamma-O'Brien, Carrasco et al. 2010), with mass production rates varying by an order of magnitude according to the initial methane concentration. The maximum is reached at intermediate methane concentrations, and is driven by methane dissociation. Methane dissociation involves indeed two opposing effects on the aerosol chemical growth: a carbon organic supply but also an increasing release of H atoms in the reactive medium (Carrasco, Gautier et al. 2012). The methane concentration in the reactive mixture also impacts the final chemical composition of the laboratory aerosols (Derenne, Coelho et al. 2012, Gautier, Carrasco et al. 2014, He and Smith 2014) and their optical properties (Quirico, Montagnac et al. 2008, Mahjoub, Carrasco et al. 2012, Brassé, Muñoz et al. 2015), suggesting an altitude-dependency of the aerosols in higher layers of Titan's atmosphere.

One of the main experimental limitations of plasma and photolytic reactors, is to reproduce Titan's high-altitude pressure conditions (lower than 10^{-4} mbar, see Figure 9) and long mean free paths for ions and neutrals in the laboratory. Indeed at these low pressures the mean free path of the reactant species has to be several orders of magnitudes lower than the smallest dimension of the reactor to prevent prominent wall effects (Carrasco, Giuliani et al. 2013). This condition involves reactors with kilometric dimensions to simulate Titan's gas-phase ionospheric chemistry, inaccessible in conventional laboratories. The higher pressures used in the plasma and photolysis setups suggest that the production of aerosols in laboratory experiments can be rather distinct from Titan ionospheric chemistry, as three body-reactions will contribute significantly to the whole chemistry network. Lower pressure plasma discharge experiments have attempted to at least run in conditions where radicals have marginal lifetimes, but the mbar type pressures (with mean free paths ~ mm) are much smaller than the conditions of Titan's ionosphere where the mean free paths are kilometers. Thissen *et al.* (2009) attempted to produce Titan chemistry at low pressures using a synchrotron source and a low pressure vessel and found some of the same reaction pathways as are observed at Titan, however an important contribution of wall-effects was observed and the nitrogen containing hydrocarbon production has remained elusive. To date no laboratory experiments have been successfully performed that replicate the pressure conditions at Titan where the complex hydrocarbons are produced.

Reactions of interest for Titan's higher atmosphere are moreover individually investigated through single collision experiments, feeding Titan's photochemical models with a bottom-up approach. The experimental setups are in this case the same as previously described for the ISM purpose (see section 2.1). A specific focus on Titan's negative ion chemistry has moreover led to an intermediate pressure regime approach in the laboratory. The progressive increase of the pressure in a ion-neutral reaction cell enabled to probe various multiple collision regimes and generate secondary products for the reaction between CN^- and HC_3N (Žabka, Romanzin et al. 2012).

4.3 Reactions in the lower Titan atmosphere

The lower atmosphere of Titan had not been observed due to dense mist before the landing of Huygens probe in 2005; it is another possible sites for abiotic synthesis of organic compounds as well as Titan's higher atmosphere. Solar UV light and electrons from magnetosphere of Jupiter are two of the major energy sources in the higher Titan atmosphere, but they cannot reach to troposphere of Titan. Thus possible energy sources for chemical reactions in troposphere would be cosmic rays and meteor impacts.

Taniuchi *et al.* (2013) examined possible formation of organic compounds in simulated Titan atmosphere by proton irradiation. A mixture of 5 % methane and 95 % nitrogen (700 Torr) was irradiated with 3 MeV protons from a van de Graaff accelerator (TIT, Japan). As soon as the irradiation started, mist was formed in gaseous phase, showing that solid materials were formed from methane and nitrogen. They can be called *Titan tholins*, though their appearance is different from *tholins* produced by plasma discharges in a low-pressure mixture of methane and nitrogen. Hereafter the solid product by proton irradiation is called *PI Titan tholins*.

PI Titan tholins have quite complex structures as suggested by FT-IR and pyrolysis GC/MS, whose average molecular weight was some hundred Dalton as estimated by gel permeation chromatography. Pyrolysis under the similar condition as performed by the Aerosol Collector and Pyrolyzer (ACP) on board Huygens Probe, NH_3 and HCN was observed as the major pyrolysis products, which was the same as the analytical results of Titan aerosol by Huygens ACP.

They could be partly dissolved with water and some organic solvents as tetrahydrofuran (THF). When PI Titan tholins were acid-hydrolyzed, a wide variety of amino acids were detected by HPLC: Glycine was predominant whose energy yield (G-value) was as high as 0.03 molecule/100 eV deposited. Such chiral amino acids as alanine, a-aminobutyric acids, valine, norvaline and aspartic acids were also detected by HPLC, and were proved to be racemic mixtures. Thus it was confirmed that the PI Titan tholins included amino acid precursors.

The present starting materials are only methane and nitrogen, which did not contain any oxygen-bearing molecules. Thus, free amino acids that contain oxygen atoms could not be formed by the irradiation. In order to examine the source of oxygen in amino acids obtained here, the PI Titan tholins were hydrolyzed with 1 M HCl prepared by dilution of concentrated HCl with $H_2{}^{18}O$, and were subjected to MALDI-MS analysis. The results that yielded amino acids mainly contained ^{18}O, not ^{16}O, showed that oxygen atoms were incorporated during hydrolysis of amino acid precursors.

Short-wavelength UV radiation cannot reach to lower atmosphere of Titan, but near UV ($\lambda > 300$ nm) could be a possible energy source of chemical reaction in troposphere of Titan. Such UV photons cannot dissociate N_2 or CH_4, but some photochemical products in stratosphere could fall down to troposphere to take part in some photochemical reactions. C_4N_2 (dicyanoacethylene) waschosen as a candidate molecule that could be supplied from stratosphere to troposphere of Titan: After photolysis of C_4N_2 yielded non-volatile haze-like materials (Gudipati et al., 2012; Couturier-Tamburelli et al., 2014).

Thus it can be said that tholins could be formed not only in Titan stratosphere but also in Titan troposphere. There tholins could be formed directly from CH_4 by cosmic rays, and also formed from such activated molecules as C_4N_2 (formed from CH_4 in stratosphere) even by near UV light.

Titan tholins synthesized under upper atmosphere by plasma discharge also yielded amino acids after acid hydrolysis (Khare *et al*. 1986). Nguyen et al. (2008) also reported that "discharge" tholins gave amino acids and carboxylic acids after acid hydrolysis. It is unlikely, however, that acid hydrolysis with strong acid occurred in Titan environment. Interaction of tholins (discharge tholins) with possible solvents in Titan environments (ammonia water and hydrocarbons) was studied. Poch et al. (2012) reported that amino acids and nucleic acid bases were formed after tholins synthesized by glow discharge in a mixture of N_2 and CH_4 (98:2) after dissolved in ammonia water. Neish et al. (2010) synthesized tholins by glow discharge in a mixture of N_2 and CH_4 (98:2). They suggested that a wide variety of amino acids and all of five nucleic acid bases were formed when the tholins were dissolve in cold cold ammonia water (253 or 293 K). In order to avoid the possibility of contamination, experiments using isotope-labelled starting materials would be favorable.

The energy flux of solar UV and electrons from Jupiter magnetosphere is much higher than that of cosmic rays. However, amino acid precursors formed in Titan lower atmosphere by cosmic rays are not ignorable since the energy yield (G-value) of amino acid precursors by proton irradiation was much higher than that of plasma discharge or UV irradiation. Both tholins formed in upper Titan atmosphere and tholins formed in lower Titan atmosphere would be supplied to Titan's surface, and could interact with surface water ice or ammonia water from subsurface ocean to yield amino acids. It is of interest to discriminate upper Titan tholins from lower Titan tholins in future Titan mission.

Besides traditional laboratory simulation experiments, a bland-new trend in simulation experiments is space experiment. By using man-made satellites, space shuttles and space stations, a wide variety of experiments including astrobiology experiments have been conducted (Horneck et al., 2010). Carrasco and co-workers (2015) placed a Titan-type gas mixture (150 kPa) of N_2, CH_4 and He (or CO_2) in cells with MgF_2 windows on an exposed facility of the International Space Station. The gas mixture was exposed to solar vacuum UV. Unsaturated hydrocarbons were detected, while conventional laboratory VUV irradiation experiments by using low-pressure gas mixtures mainly yielded unsaturated hydrocarbons: The difference in gaseous pressure would have caused it. It is of interest to repeat such space experiments to see synergetic effects of solar UV and cosmic rays in chemical evolution.

Tholins formed in Titan atmosphere containing methane would be partly dissolved in liquid ethane-methane lakes found on Titan (Brown et al., 2008). We have quite limited knowledge how tholins would behave when dissolved in cold hydrocarbon lakes. It will be of great interest to simulate possible chemical evolution of tholins in liquid methane-ethane lake of Titan.

4.4 Origins of methane in the outer solar system

The number of experiments dedicated to the investigation of methane chemistry is scarce in other planetary environments, and essentially dedicated to the investigation of the methane formation conditions via Fischer-Tropsch-Type (FTT) reactions. For example, in order to investigate the origin of Titan's atmospheric methane, Sekine *et al.* (2005) conducted FTT experiments in low pressure and low temperature ranges corresponding to the thermodynamic conditions occurring in the protosolar nebula and in circumplanetary disks such as the Saturn's subnebula. They thus showed that the FTT catalysis is efficient in a narrow temperature range (~500-600 K) in the gas phase conditions of the protosolar nebula or Saturn's subnebula and can be used to trace back the evolution of CO and CO_2 in these environments. The experimental results of Sekine *et al.* (2005) suggest that these two species are converted into CH_4 within time significantly shorter than the lifetime of the solar nebula at the optimal temperatures around 550 K. These authors thus concluded that CH_4-rich satellitesimals could have formed in the catalytically-active region of the subnebula and thus may have played an important role in the origin of Titan's atmosphere. Despite of the fact that these experiments suggest that Titan's atmospheric methane could have been produced in the gas phase of Saturn's subnebula, they are not found consistent with the high D/H ratio measured of this molecule, which is found to be ~6 times the protosolar value (Bézard *et al*., 2007). On the contrary, the D/H in CH_4 produced in the Saturn's subnebula should be very close to the protosolar value (Mousis *et al*. 2002), thus invalidating the idea that this molecule was formed from CO and protosolar H_2 in Saturn's subnebula. The only scenario that remains consistent with this constraint is that CH_4 was originally formed in the Interstellar Medium and subsquently accreted in Titan's building blocks in the protosolar nebula (Mousis *et al.*, 2009).

Interestingly, Enceladus is a good candidate for the existence of serpentinization and FTT reactions in its interior. The plumes of vapor and water ice particles rich in sodium salts erupting from the south polar region of Enceladus suggest the presence of a liquid water reservoir below the crust (Potsberg *et al*., 2009, 2011; Waite *et al*., 2009). Moreover, the recent discovery of silicate nanoparticles derived from the plumes by the Cassini spacecraft indicates the presence of rocks in contact with Enceladus' ocean (Hsu *et al.*, 2014). These observations are complimented by the observations of CH_4 in Enceladus' plumes (Waite *et al*., 2009). According to laboratory experiments (Sloan and Koh, 2008; Vu and Choukroun, 2015), methane clathration should be very efficient in the internal ocean and suggests that methane should be at very low concentrations in the plume. A simple way around this is to have active production of methane via water-rock interactions (Bouquet et al., 2015). This has motivated a new interest in conducting serpentinization experiments in the appropriate temperature and pressure ranges (Sekine *et al*., 2014).

5. Conclusion and future prospects

Methane is the simplest hydrocarbon and can be observed in a wide variety of extraterrestrial environments, including interstellar space and atmospheres of gas giants and Titan. Both methane formation processes and further reactions from methane have been studied both by theoretical calculations and simulation experiments.

In order to simulate interstellar gaseous reactions, experiments are performed under low pressure, including those done with CRESU. In addition to the gas phase, reactions on the surfaces of ice mantles of interstellar dust particles (ISDs) should not be ignored. A possible formation pathway of methane is the addition of H atoms to C atoms on dust surfaces. This pathway has not been unambiguously established experimentally, but the formation of CH_3OH from CO via HCHO has been experimentally confirmed.

Another series of experiments involve the synthesis of complex organic compounds from possible molecules in the ice mantles of ISDs. Ultraviolet light and cosmic rays are two possible energy sources, and complex molecules including amino acid precursors were formed from such icy mixtures. In these experiments, CO and/or CH_3OH were mainly used as carbon sources, and amino acid precursors were formed. When methane was used as a sole carbon source, however, amino acid precursors hardly were formed by UV irradiation. The role of methane in the ice mantles in the formation of complex molecules should be examined in future experiments.

In the mid-20th century, a strongly reducing primitive Earth atmosphere containing high concentration of methane was postulated, and a great number of experiments were conducted: The presence of such an atmosphere was disproved later, but methane might have presented as a minor constituent. Even now, a supply of a small amount of methane is observed in submarine hydrothermal systems. Chemical evolution in such submarine hydrothermal systems has been studied not only theoretically but also experimentally. Several research groups used not only closed autoclaves but also flow reactors and the latter could show importance of quenching processes in hydrothermal systems. Methane was often used in autoclave experiments to pressurize the system, but little flow reactor work has been performed with methane gas. It would also be of interest to see the roles of methane in reactions in flow reactors.

Titan, having a dense atmosphere containing methane, is considered as a natural laboratory of chemical evolution. A wide variety of laboratory experiments have been performed to simulate higher or lower atmosphere of Titan with various energies such as solar UV, electrons in Saturnian magnetosphere and cosmic rays. It has been shown that complex solid organics sometimes referred to as *tholins* were formed in these simulation experiments, which corresponded to haze in Titan atmosphere observed in Cassini-Huygens mission. Another important topic concerning methane in Titan is finding of liquid ethane-methane lakes on Titan. These tholins were sometimes discussed in the context of a possible generation of life in Titan's liquidosphere. Possible chemical evolution in that environment could be studied by simulation experiments, which would be important to design future Titan missions.

Not only Titan but also other icy bodies such as Enceladus and Pluto would be good targets to understand the diversified methane chemistry in space, and experiments simulating environments of these bodies are expected.

There have been a great number of experiments examining the chemistry of methane and related molecules in various environments. However, there has been little collaboration among research teams involved in such experiements. For example, experiments simulating surface reactions on ISD ice mantles have been conducted mostly independently from those modeling photochemical / radiochemical reactions in those mantles. Further interdisciplinary collaborative work among different research groups is therefore desired. Furthermore, it is of extreme interest to formulate an overall synthesis scenario from interstellar molecules to prebiotic molecules, including the possible environmemnts of terrestrial submarine hydrothermal systems or in Titan hydrocarbon lakes.

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FIGURE CAPTIONS

FIG. 1. Basic scheme of a selected ion flow tube apparatus, which consists of an ion source, a quadrupole mass filter to isolate a given ion reactant, the reaction zone, where neutral species are introduced, and a quadrupole filter/ channeltron product analyzer (from Smith and Adams 1988).

FIG. 2. Schematics of a Flowing afterglow apparatus. Ions (and electrons) are produced in the microwave discharges. By means of introduction of a reactant secondary ions can be produced. With the movable Langmuir probe the decay of electrons through recombination reaction can be followed. Taken from Larsson et al. 2012.

FIG. 3. The CRYRING magnetic storage ring. Ions are produced in the MINIS ion source and injected into the ring *via* a radiofrequency quadrupole. After acceleration in the ring by a radiofrequency field the ion beam is merged with an electron beam in the electron cooler. Neutral products of ion-electron reactions are unaffected by the magnetic field and leave the ring tangentially and can be detected by the surface barrier detector. Taken from Larsson et al. 2012.

FIG. 4. Schematic of the CRESU apparatus. Reactants are produced from the precursor in the moveable reservoir and enter the vacuum chamber in a supersonic flow of the carrier gas through the Laval nozzle. The decay of the reactant is followed by means of Laser induced fluorescence by the photomultiplier (PMT). The variable distance between the reservoir and the detector allows to observe the intensity of the reactant in the supersonic flow at different flow times. Taken from Smith (2006).

FIG. 5. Normalized column density of CH_4 as a function of irradiation dose (eV/16u) after ion bombardment of pure CH_4 and a H_2O:CH_4=4:1 mixture at 12 K with 30 keV He^+.

FIG. 6. Top panel: Normalized column density of CH_3OH as a function of irradiation dose (eV/16u) after ion bombardment of pure CH_3OH and two mixtures, $CO:CH_3OH$ and $N_2:CH_3OH$, at 16 K with 200 keV H^+. Bottom panel: Column density of CH_4 formed at 16 K after ion bombardment (200 keV H^+) of the same CH_3OH-rich ice mixtures divided by the column density of CH_3OH at the same dose.

FIG. 7. Comparison between observed and laboratory spectra. Data points are ISO observations. Thin solid lines are laboratory s is the best-fit to the observed data points obtained by a linear combination of two laboratory spectra. The thin lines are the laboratory spectra scaled by the coefficient given by the fit procedure.

FIG. 8. Schematically introduction of the CAPS and INMS data sets that have been used to study the ion-neutral chemistry producing complex organic compounds in Titan's upper atmosphere. Panel A shows the neutral (upper) and ion (lower) mass spectra from 1 to 100 u in Ttian's upper atmosphere. Panel B shows the mass spectra from Crary et al. (201?) taken by CAPS IBS and indicating positive ions that contain PAHs and nitrogen substituted aromatics that extend to >250 u. Panel C is a negative ion spectrum from Coates et al. (201?) indicating that the ion neutral chemistry also involves negative ions with masses of over 5000 u.

FIG. 9. The pressure regime of tholin laboratory experiments versus the in situ pressure conditions measured by Cassini-Huygens. Ion neutral organic fomation processes dominate at low pressures, whereas radical three body stabilized reactions predominate at higher pressures.