

Laboratory Studies Towards Understanding Comets

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Abstract This review presents some of the recent advancements in our understanding of comets facilitated by laboratory studies, need for new laboratory simulations, and predictions for future explorations. With the spacecraft Rosetta at the comet 67P/Churyumov–Gerasimenko, a large volume of science data is expected to follow early results that have been published recently. The most surprising of them being hard ice shell that bounced the lander Philae a couple of times before settling on the comet. Long evaded molecular nitrogen has now been detected in the comet 67P/CG. The observed density of 470 kg m^{-3} is in line with other comet observations, whereas the nature and composition of hydrocarbons

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detected on the surface are still a puzzle. Observation of D/H ratio that deviates significantly from Earth's water D/H ratio brings back to the table the long-standing question whether or not water on Earth was delivered by comet impacts. Our review summarizes some of the critical laboratory work that helps improve our understanding of cometary interior (whether amorphous or crystalline or containing clathrates), cometary surface (rich of complex organics), cometary coma and tail (D/H ratio, negative ions, and photoluminescence). Outstanding questions are also discussed.

Keywords Comets · Laboratory · Experimental · Ice · Volatiles · Clathrates · Origin of life · Organics · Review · Isotope ratios · Negative ions · Coma · Outgassing · Origin of solar systems

1 Introduction

There are excellent reviews (A'Hearn 2011; Bockelée-Morvan 2010; Lisse et al. 2013; Mumma and Charnley 2011) and books (Festou et al. 2004) or book chapters on comets, their anatomy, physics, chemistry, and dynamics. More popular books on comets are also emerging (Eicher 2013) to reach out to the curiosity of majority of the humans, who inevitably would have seen or will see a comet in their lifetime. In brief, comets are icy bodies with all sizes (kilometers diameter/length) and shapes, highly porous, mostly with dark surface and have highly eccentric orbit around the Sun. When comets get closer to the Sun, their surface temperature increases resulting in outgassing of volatiles, flow of jets containing molecules, ions, and dust/ice particles, all of which become a comet's coma and subsequently tail of a comet that spans for hundreds of thousands of kilometers. Comets originate from either the Kuiper Belt or Oort cloud. In either case, comets are supposed to contain and preserve the most primitive (primordial) ice, dust, and organics from interstellar medium that would have gravitationally collapsed into a dense molecular cloud and subsequently to a protostar, whose ice-line kept the KBOs and Oort cloud objects unaltered in their interior (Irvine et al. 1996; Wooden 2008). Thus, the connection between comets and interstellar ice grains is critical to understand. Also important is the role of comets (and asteroids) in the origin of life on Earth, as the earliest organisms seem to have emerged about 3.8 Gyr ago (Fedou et al. 2006), soon after the late heavy bombardment (Bottke et al. 2012; Broz et al. 2013; Gomes et al. 2005) around 4.1–3.8 Gyr ago.

Molecular and atomic composition of cometary coma/tail is relatively well studied and understood (Lisse et al. 2005; Moreno et al. 2003; Mumma and Charnley 2011), but their origin—whether outgassing or photochemical or both still needs clarification. Nature of charged species in cometary coma needs a better understanding as well. Surfaces of short-period Jupiter family comets do not show permanent/significant water-ice presence, whereas refrosting could occur on some parts and can be seen at large incidence angles at the morning side as patches of water-ice that is not intimately mixed with the surface dust (Groussin et al. 2013). Cometary surface is thus expected to be composed of non-volatile refractory organics and silicate grains. Thickness of this surface crust is an unknown still and it is not clear how deep is water-ice buried (centimeters to meters). Several models discuss the cometary interior composition and thermal properties (Davidsson et al. 2013; Prrialnik 2002), some involving amorphous ice grains and others ignoring the water-ice phase (Gortsas et al. 2011; Kuhrt 1999). There is a general conscience that comets are highly porous (porosity >50 %), low density ($\sim 0.3\text{--}0.6 \text{ g/cm}^3$), and poor thermal conductors with low thermal inertia of $\sim 10\text{--}50 \text{ JK}^{-1} \text{ m}^{-2} \text{ s}^{-0.5}$ (Gulkis et al. 2015). It is not clear whether the interior of

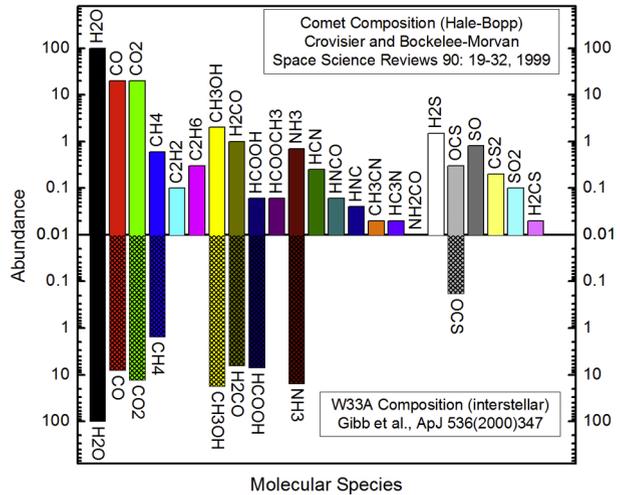
a comet is composed of small grains (micron-size) or a wide distribution of grains, rubble, and blocks. It is not clear whether the interstellar ice grain composition (Greenberg 1963), containing large amount of volatiles trapped in amorphous ice, is retained and preserved in a comet's nucleus. Outgassing of a comet typically begins close to 3 au (where the daytime temperature starts raising beyond 180 K). Carbon monoxide is seen early in the formation of a cometary coma—so called “lighting up the comet” during a comet's journey towards perihelion. Is this CO from the subsurface, trapped within amorphous ice or trapped in the grain boundaries of loosely bound crystalline ice grains, or photochemically made from the surface refractory organics? What is the chemical composition of organics in cometary tail—charged and neutral? How this composition connected to surface and interior composition of a comet? These are only a few samples of a suit of questions for which laboratory studies (in collaboration with modeling and observational studies) would help find answers. In this review article we try to bring as many of these questions/answers/predictions/postulates as possible by focusing on the laboratory studies to address the four parts of a comet: interior, surface, outgassing, and coma. The review is also structured into the same four parts. First we discuss briefly the outstanding questions for which laboratory studies are urgently needed and then we present some of the studies that helped resolve ongoing and past observations.

2 Motivation for Laboratory Studies

The pool of solar system icy bodies (Kuiper Belt Objects and Oort Cloud), where comets are known to originate from, are thought to be the least processed presolar material left behind. Comets are exposed to extreme variations in temperature and solar radiation; as a consequence, a comets surface, coma, and tail are intimately connected to its interior make up, which is a challenge even today to understand. A comparison of interstellar ice grain composition (in the solid phase) and a comet's volatile coma composition (outgassing) is shown in Fig. 1. The data is normalized to water abundance. This bar plot helps visualize the fact that many species in cometary outgassing are very similar in abundance as compared to the interstellar ices, indicating that the composition of volatiles is preserved. Cometary coma shows far more oxidized species that have not (yet) been identified or detected in interstellar ice grains. We should keep in mind that the only spectroscopic method so far used to study interstellar ice grains is the infrared absorption in the mid-IR region, where many species could have overlapping IR absorptions (unresolved) or their absorption could be weak and buried under strongly absorbing molecular species. On the other hand, in cometary coma/tail, each molecule is observed through a variety of spectroscopic techniques (infrared, microwave/far infrared, ultraviolet, etc.), and in the gas-phase these molecules show much sharper absorption profiles, avoiding overlapping bands. At this juncture it is not clear whether the interstellar ice grains lack the diversity of oxidation products seen in cometary outgassing or whether it is merely a limitation of the observational methods. Laboratory studies presented in Sect. 3 deal with complex chemistry that could occur in presolar conditions and properties of volatiles trapped in amorphous ice vs. crystalline ice containing clathrates of volatiles in a comet's interior.

Thanks to recent missions to comets, we have unprecedented volume of data on the surface topography and geology of comets. While most of the cometary surface material is suggested to be organic crust and dust mix—resulting in a low albedo material, the exact composition of a cometary surface, its thickness, its thermal conductivity, its gas permeability, and its photochemical activity—are still far from well understood. Microwave instrument for the Rosetta orbiter (MIRO) of Rosetta mission has shown that the thermal inertia of

Fig. 1 Molecular abundances of comet outgassing (Hale-Bopp) compared with interstellar ice composition (W33A). A striking similarity among the major volatile species can be seen, indicating that interstellar ice grain composition is preserved to a greater extent in comets



comet 67P/CG is very low and within a few centimeters the temperature could significantly fall several tens of K (Gulakis et al. 2015), consistent with a thermally insulating powdered surface. Laboratory experiments are gaining momentum in simulating the surfaces, how the surface reacts to extreme temperature changes, radiation, and volatiles from the interior are some of the few examples of what needs to be addressed in the lab. Along these lines, recent studies (Lignell and Gudipati 2015) subjecting cometary ice analogs to thermal cycles revealed that phase separation occurs between amorphous ice that crystallizes, expelling the impurity organics that form the outer crust. These laboratory studies are in agreement with recent Rosetta observations that hard crust (likely crystalline ice) is covered with organic dust. Some of the laboratory studies may have to look for observations/modeling to find answers. Understanding the physical properties of cometary analogues provides the possibility to better constrain the conditions under which comets have formed. For example, the water-driven dust activity of comets can only be explained if comets were to be formed by gravitational instability (see Sect. 4.1). Rosetta's VIRTIS (visible and infrared thermal imaging spectrometer) has clearly shown that a comets surface is rich with organics. We do not yet exactly know what kind of organics these are and whether they are intimately mixed with silicate grains and what ratio these two materials have at different heliocentric distances of a comet, these are all unknowns.

Section 4 deals with radiation-induced chemical evolution of simple organic volatiles shown in Fig. 1. Production of complex non-volatile organics as well as potential biologically relevant prebiotic organics is observed under laboratory conditions. In the laboratory, irradiation by UV photons or charged particles followed by thermal heating of astrophysical ice analogues that contain simple molecules such as H₂O, CH₃OH, NH₃ and CO₂ have produced a suite of complex organic molecules similar to those found in small bodies of our Solar system. When UV photons penetrate into ices, they break bonds, producing radicals and activated species, which during warm up lead to the formation of photoproducts. Diffusion and reaction barriers control this radiation-induced chemistry in cometary and astrophysical ices. As a result a suit of complex organics are synthesized on cometary surface and near surface, of which some of them volatile and others refractory (organic compounds with a larger desorption energy than water). Refractory residue analyses have shown an important molecular diversity with interesting similarities with the soluble or insoluble organic matter found in carbonaceous meteorites. Investigation of the formation mechanisms

of the most abundant molecules present in refractory residues is an important challenge that can drive the search for these species in cometary environments. Accordingly a mechanistic approach of cometary reactivity has been developed on polyoxymethylene (POM) and hexamethyltetramine (HMT) two molecular compounds detected in the organic residue that will be searched for by the Rosetta instruments. These experiments give constraint on cometary environment in which they can be search for as well as on the possibility to detect them by instruments on-board of the Rosetta mission. Characterization of the volatile species is also important, since they certainly take a part in the subsequent formation of these refractory residues, and give a screening of molecules desorbing during a comet heating.

Section 5 is devoted to volatiles outgassed during perihelion approach of a comet, which are the most studied due to their access for ground and space based observatories. As a comet approaches its perihelion, its surface temperature increases resulting in sublimation of atoms and molecules from its surface (non directional). This sublimation forms the coma of a comet and subsequently evolves into comet's tail. As the temperature increases with decreasing distance to the Sun, jets containing both gas and dust/ice grains are routinely observed. Very few laboratory studies are available that focus on the jets of a comet (Laufer et al. 2013), where as extensive work is focused on understanding the coma and tail—through the outgassing process.

One of these studies involves D/H ratios of cometary water in order to connect it with presolar ice grains and whether or not comets delivered water on Earth during the early stages of our solar system. The formation of water on dust grains in the interstellar medium at very low temperatures favors heavier isotopes. Very high deuterium enrichments in protostellar envelopes with D/H ratios of about 0.1 % and 1 % were reported by Butner et al. (2007) and Ceccarelli et al. (2005) respectively. This is a factor 50 to 500 higher than the D/H ratio of protosolar hydrogen (21 ppm). Isotopic exchange processes in the inner protoplanetary disk under temperatures between 600 and 1300 K and pressures between 10 μ bar and 1 mbar (see e.g. Yang et al. 2013) would lead to a defractionation of highly deuterium-enriched water to the hydrogen D/H ratio of 21 ppm (“equilibrated water”). With increasing heliocentric distance the efficiency of the defractionation process decreases on the one hand, and mixing processes with highly deuterated water vapor lead to an increase of the D/H ratio on the other hand. The degree of the D/H ratio increase with heliocentric distance in models (e.g. Drouart et al. 1999; Mousis et al. 2000; Horner et al. 2007 and Kavelaars et al. 2011) can be constrained by observations of the D/H ratio in comets. In the “classical” view, the Oort cloud comets (OCCs) have formed in the vicinity of the gas giants while Jupiter family comets (JFCs) at larger heliocentric distances in the Kuiper belt and scattered disk. Therefore the models predict higher D/H ratios for JFCs than for OCCs. Observations in OCCs (Balsiger et al. 1995; Eberhardt et al. 1995; Biver et al. 2006; Bockelée-Morvan et al. 1998 and 2012; Meier et al. 1998; Hutsemékers et al. 2008; Villanueva et al. 2009) reveal D/H ratios between 206 and 409 ppm, while recent observations in JFCs show values between 161 ppm (Hartogh et al. 2011) and below 200 ppm (Lis et al. 2013), i.e. the opposite of the model predictions. Based on these new constraints, recent models addressing the topic of the D/H distribution in the solar system suggest a possible overlap of the OCC and JFC formation region (Albertsson et al. 2014) or that the defractionation process happened already while the disk was still forming. In the latter case transport of defractionated water from the inner disk outwards would compensate angular momentum from still infalling material (Yang et al. 2013). The discrepancy between prediction and observation may also be interpreted in terms of the Grand Tack scenario (Walsh et al. 2011) along with the migration of the gas giants and related mixing of material over large heliocentric distances or the interpretation of Hogerheijde et al. (2011)

based on measurements of the ortho-to-para ratio of water in the nearest classical T-Tauri stellar system that comets contain heterogeneous ice mixtures collected across the entire solar nebula during the early stages of planetary birth. If true one should expect a large range of D/H ratios in each single comet and depending of its formation history related to processes of the disk formation and evolution a more or less distinct variability of the D/H ratio in cometary comas during their presence in the inner solar system. Unfortunately all existing D/H observations in comet have been performed only during a single orbital phase so that no constraints about this hypothesis exist yet. This situation will change with the on-going Rosetta mission where water D/H ratios in the JFC 67P/Churyumov-Gerasimenko will be determined continuously over heliocentric distances of at least between 1.3 to 3.7 AU. First results from ROSINA (*Rosetta* Orbiter Spectrometer for Ion and Neutral Analysis) instrument measurements on 67P/CG outgassing put the earlier theories that water on Earth has similar D/H ratios as the cometary bodies to question (Altwegg et al. 2015). As discussed in Sect. 5, more systematic and rigorous laboratory studies are needed that help understand the evolution of D/H ratios with thermal and photochemical processing connecting gas-phase D/H ratios with solid-phase composition.

Section 6 is devoted to the understanding of molecular composition of cometary coma and tail. Ionic species that form jets in a comet gas tail, especially the negative ions, that is directed away from the Sun, are somewhat less understood (Meech et al. 2005; Mumma and Charnley 2011) compared to the neutral gas and dust in a cometary tail. Negative ions could help understand the production mechanism of photoelectrons, their energies, and atomic and molecular composition of the comet itself. Finally, some of the outgassing atoms and molecules are highly fluorescent such as the polycyclic aromatic hydrocarbons (PAHs), some of them observed in cometary tails. Molecular fluorescence excited by solar radiation could contribute to understand the composition of comet coma and tail, connecting this composition back to the surface and interior composition of a comet.

3 Comet Interior

The nucleus of a comet is the invisible elephant in the room. Results from the Comet Nucleus Sounding Experiment by Radiowave Transmission (CONSERT) instrument of Rosetta mission to comet 67P/CG would soon shed some new light on the interior of a comet (Hegler et al. 2013). We have a reasonable constraints on the density of a comet ($0.2\text{--}0.6\text{ g cm}^{-3}$), meaning it is a highly porous water-ice and organic-volatile rich body mixed with silicate/mineral dust grains. Rosetta mission has determined (Sierks et al. 2015) the density of the comet 67P/CG to be 470 kg cm^{-3} , well within the above-mentioned range. However, we have very little data on the interior structure, whether it is uniform throughout or whether it consists of rock-like high-density boulders or fresh-snow like ultra-low-density regions or a mix of gradients in between. We explore in this section some of the laboratory work pertinent to a comet's nucleus. We presently have reasonable understanding of ices and volatile mixes, but studies are only emerging on the inclusion of dust (silicate/mineral grains) in the mixtures. One of the outstanding issues of cometary nucleus is the phase of water ice in the core—amorphous or crystalline (Sect. 3.1)? It is likely that the crust of a comet would have crystalline ice due to its exposure to higher temperatures than $\sim 130\text{ K}$ for a prolonged period of time. In the crystalline ice regions of a comet clathrate hydrates become important (Sect. 3.2). One should not confuse crystalline clathrates with amorphous ices with trapped volatiles, which are called “gas-laden amorphous ices”.

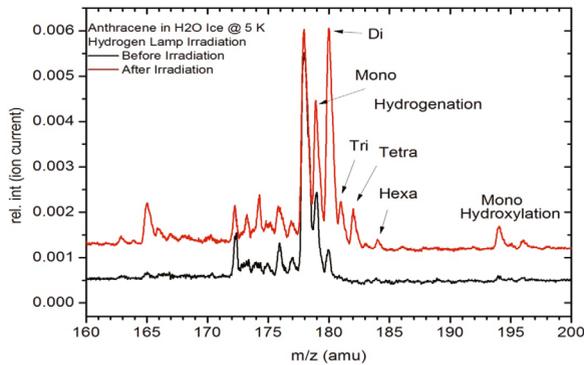
3.1 Is Present-Day Comet's Interior Made of Amorphous or Crystalline Ice?

While interstellar ice grains are predominantly made of amorphous ice (Öberg et al. 2011), most of the solar system icy surfaces are detected to be made of crystalline ice, including some of the KBOs (Brown et al. 2012a; Licandro et al. 2006). One of the key questions pertinent to comets is: What is the ice composition of a comet's nucleus interior: amorphous or crystalline? If amorphous, then why most of the KBOs have crystalline ice surface? If crystalline (interior), when did the phase-transition from amorphous to crystalline occur—during the protostar phase, or during the past 4.5 Gyr evolution? Can volatiles be trapped in the crystalline ice grains—such as clathrates—to the same extent as the amorphous ices, which are known to trap large amount of volatiles (Laufer et al. 2013; Laufer et al. 1987)? We will discuss here pros and cons for a cometary interior to be amorphous or crystalline by comparing the existing experimental and observational evidence. Eventually only a cryogenic (<50 K) comet subsurface sample analysis and return (CCSSAR—pronounced as Caesar) would answer the ultimate question: Do the comets carry the primordial interstellar ice grains in their pristine form?

Gudipati and coworkers recently developed a 2-color laser ablation and laser ionization mass spectrometry (2C-LAIMS) method, whereby ice was resonantly excited in the OH vibrations in ice at 2.94 microns to efficiently ablate the ice into the gas-phase, ionize the gas-phase atoms, molecules and clusters using a UV laser, and analyze the species with a time-of-flight mass spectrometer, in order to determine the chemical composition of the ice at any given temperature without having to heat the sample (Gudipati and Yang 2012; Henderson and Gudipati 2014, 2015; Yang and Gudipati 2014). This method, based on the pioneering work by Zare and Clemett on laser desorption mass spectrometry (Clemett et al. 1991), complements the other in situ spectroscopic techniques such as infrared, Raman, UV, and fluorescence (Allodi et al. 2013). As shown in Fig. 2, these studies clearly showed that under radiation (UV or electron) organic impurities in ices undergo complex chemistry even under interstellar temperatures (~5 K), which means it is very likely that the interstellar ice grains may host far more diverse molecular species than so far observed either in the dense molecular cloud phase or during the protostar stage, without annealing the ices to crystalline phase. These complex organics could have been preserved further during the formation of KBO and Oort Cloud icy bodies. Similar work is being pursued by several other researchers using laser-desorption mass spectrometry methods (Bennett et al. 2011; Maity et al. 2015).

One may quickly conclude: because the interstellar ice grains are made of amorphous ices, because the amorphous ices can accommodate large amount of impurities, and because cometary outgassing volatiles are strikingly similar to interstellar ice grain composition, cometary nucleus should consist of amorphous ice grains and the primordial interstellar composition should have been preserved in cometary nucleus. However, there are some modeling studies that do not consider amorphous form to be necessary (Gortsas et al. 2011; Kührt 1999) and comet interior consisting of volatiles trapped in crystalline ice clathrates are proposed (Marboeuf et al. 2012a, 2012b; Mousis et al. 2015) challenging the amorphous ice interior hypothesis.

Most of the comet nucleus thermal models do not ask the question whether the interior ice is amorphous or crystalline, rather these models use thermal conductivity as a proxy for porosity—whether amorphous or crystalline in nature. Thermal conductivity of amorphous ice (with or without impurities) is not constrained in the laboratory (Andersson and Inaba 2005; Andersson and Suga 2002; Bar-Nun and Laufer 2003; English et al. 2010; Handa et al. 1986; Kouchi et al. 1992; Waluyo et al. 2008), whereas these values are well constrained for



Irradiation Products of Single and Dual-Component Ices, 5 K

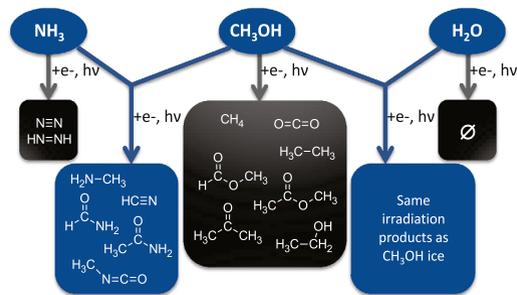


Fig. 2 *Top*: Two-color, two-step laser and ablation (laser) ionization mass spectra (2S-LAIMS) of a polycyclic aromatic hydrocarbon (PAH) anthracene ($C_{14}H_{10}$) in H_2O ice at 5 K before (*black curve*) and after (*red curve*) Lyman- α UV radiation processing at 5 K. Mass peaks due to hydrogenation (up to 8) and hydroxylation (one) can clearly be seen in the mass spectrum measured after radiation processing at 5K indicating complex radiation chemistry involving organics and water matrix can occur even in the coldest parts of the Universe, including interstellar ice grains that eventually transform to outer solar system and cometary nucleus. Reproduced partly from (Gudipati and Yang 2012). *Bottom*: Complex organics, including some key prebiotic molecules produced from radiation processed interstellar and cometary ice analogs investigated using the 2S-LAIMS methodology. Reproduced from Henderson and Gudipati (2015)

crystalline ice at cryogenic temperatures (Andersson and Inaba 2005; Hansen and McCord 2004; Kim et al. 2003; Smith et al. 2003). Thermal conductivity, porosity, grain size, dust (silicate) grain composition, and volatile fraction—all these parameters are correlated to each other in modeling a cometary interior thermal inertia. One of these models proposes that crystalline ice properties could be used to compute thermal properties of a comet as well as its outgassing behavior (Gortsas et al. 2011), which puts a fly in the ointment. Is this possible that cometary nucleus could be composed of crystalline ice and still behave very similar in each orbit from aphelion to perihelion and back—with respect to outgassing volatiles (with similar number density)? Or is it only that in the upper crust of a comet (a few cm to a few meters—to be constrained) ice becomes crystalline, leaving the interior to be amorphous? A short period comet's aphelion is ~ 5 au (Jupiter), leaving the minimum surface temperature to be ~ 120 K in the daytime. Could this be sufficient to crystallize the interior ice of a ~ 1 km diameter comet? These are the questions for which we still lack credible experimental data and theoretical models (that rely heavily on experimental data).

Yet another important aspect of amorphous or crystalline ice is the laboratory work on pure water-ice may not always represent water-ice heavily loaded with trapped species. In

fact, both in comets and interstellar ice grains though water alone is the most abundant molecule, when the abundances of all the organic impurities are added together, then water to total impurity ratio is almost 1:1 (see Fig. 1). So, cometary interior must have a mechanism to trap extremely high quantity of organic volatile impurity, and still maintain a high porosity to get overall density to be $\sim 0.2\text{--}0.4 \text{ g cm}^{-3}$ (Thomas et al. 2013). Laboratory studies show that while pure amorphous water ice undergoes exothermic (releasing heat) crystallization at higher temperatures, crystallization of amorphous ice with impurities trapped is an endothermic (takes heat) process (Kouchi and Sirono 2001). Though quantitative data on heat of crystallization of impurity-laden amorphous ices still need to be obtained in the laboratory, if true and if the magnitude of endothermic heat consumption to be significant, spontaneous break-up of comets can no longer be attributed to runaway crystallization process. Further, it is necessary that at one or other point in the history of a comet's life, there should have been sufficient heat deposited into the interior with very poor thermal conductivity, in order to make the amorphous to crystalline transition—adding another barrier to spontaneous crystallization that has so far been assumed in the literature. Implications of this endothermic crystallization of amorphous ices would include retention of primordial interstellar ice composition in the interior and much closer to the surface than so far thought.

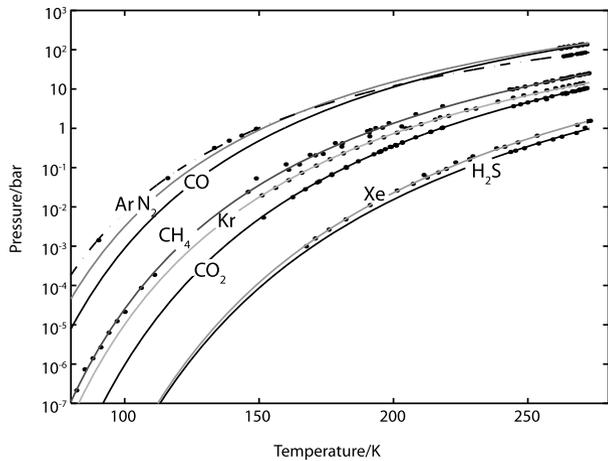
More laboratory work on physical properties such as thermal conductivity, heat of crystallization, and thermal and photochemical processes in amorphous ices containing impurities is critical to constrain our understanding of a comet's interior. At the same time more laboratory data is needed on crystalline ice generated from amorphous ice annealing or directly made at higher temperatures, its volatiles trapping abilities. Another mechanism for trapping volatiles is in the form of clathrates and hydrates. Some work is done in the laboratory on high-pressure generated clathrates and their relevance to astrophysical and cometary ices (Dartois et al. 2013; Dartois and Deboffle 2008). Laboratory work on low-temperature and low-pressure clathrates (molecules trapped in crystalline ice) would lead us to a better understanding of the role of crystalline ices under low-gravity, low-pressure, and low-temperature conditions, as discussed in the next section.

3.2 Role of Clathrates: Formation, Equilibrium Conditions, and Composition of Clathrate

Clathrate hydrates (hereafter clathrates) are ice-like crystalline solids forming from water and non-stoichiometric amounts of small non-polar molecules under appropriate conditions of temperature and pressure. Water molecules form cages or cavities, which may, or may not, contain guest molecules. To be stable, clathrate structures require that a minimum amount of guest molecules be trapped into the cages without forming any covalent or hydrogen bonds to the water molecules. The most common guest molecules engaged in terrestrial clathrates are of organic aliphatic nature like methane, ethane or propane. However other small inorganic molecules like carbon dioxide and nitrogen can also be engaged in clathrates. Clathrates are considered today as one of the most important reservoirs of fossil energy on Earth (Sloan and Koh 2008). The two most common clathrate structures known in natural environments are “structure I” and “structure II”. In structure I, the unit cell consists of 46 water molecules and can trap up to 8 guest molecules. In structure II, the unit cell is composed of 136 water molecules and can incorporate 24 guest molecules at most.

Of particular interest is the clathrate structure that can incorporate volatile molecules from the surrounding gas phase in the water ice structure during the course of the cooling of the protosolar nebula. This structure of water ice can cause chemical fractionation of the

Fig. 3 Equilibrium pressure of single guest clathrates of CO, CO₂, CH₄, H₂S, N₂, Xe, Kr, and Ar. Dots are experimental data and *solid lines* are fits using Eq. (1). See Fray et al. (2010), Marboeuf et al. (2012a), Mohammadi and Anderson (2010, 2011, 2013) for further details on the experimental data



trace gases, depending on various parameters such as ambient temperature, pressure, and chemistry. Here, we discuss the formation of clathrates at low pressure ($\ll 1$ bar) and low temperature ($\ll 270$ K) under laboratory conditions. We also review the accessible data representing the equilibrium conditions of species that have significant relevance for cometary environments. Experiments showing the fractionation of gaseous mixtures once trapped in clathrates are also depicted. Because of the scarce number of experimental data regarding the equilibrium and composition of clathrates formed at low temperature and pressure conditions, we finally discuss the assumptions made in models computing the formation conditions and composition of icy planetesimals condensed in the protosolar nebula.

3.2.1 Review of Existing Experiments

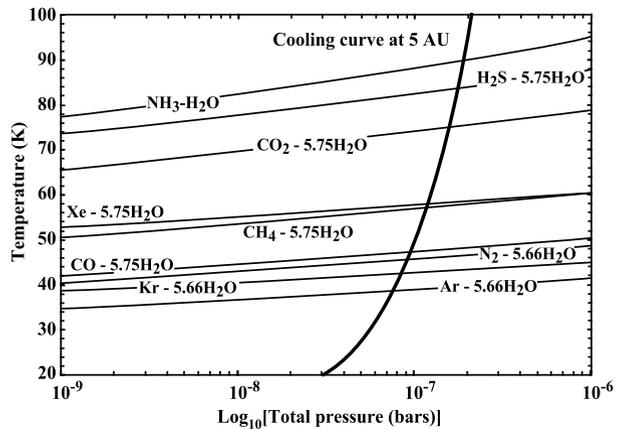
Clathrates are composed of a cubic structure of water ice that forms cages within which guest molecules, initially in the gas phase, are trapped by Van der Waals forces. The formation/dissociation of clathrates at the surface of icy grains in the protosolar nebula or in comets occurs by gas-water ice interaction. The equilibrium pressure of guest molecules defines the stability of this structure. At a given temperature, the cages are stable as long as the pressure of the gas phase is equal to or greater than the dissociation pressure of the clathrate structure. Below the equilibrium gas pressure of the guest molecule, the cages become unstable and dissociate, leaving only the water ice and volatile molecules in the gas phase. Numerous experimental studies determined the equilibrium pressure of single guest clathrate hydrates for several molecules (see Fig. 3). The clathrate equilibrium conditions are usually depicted via an Arrhenius-type law:

$$\ln(P^{cl}(x)) = A_0(x) + A_1(x)/T, \quad (1)$$

where $P^{cl}(x)$ is the equilibrium pressure of the guest molecule x expressed in bar and T in K. $A_0(x)$ and $A_1(x)$ are constant parameters that depend on the nature of the guest molecule x (see values in Hersant et al. 2004; Fray et al. 2010; Marboeuf et al. 2012a and references therein).

Among the large list of clathrate forming volatiles, a dozen of guest species are of particular interest in planetary science: CO, CO₂, CH₄, CH₃OH, N₂, NH₃, H₂S, Xe, Kr, and Ar. Except N₂ and Xe, Kr and Ar, these molecules are the most abundant volatile species

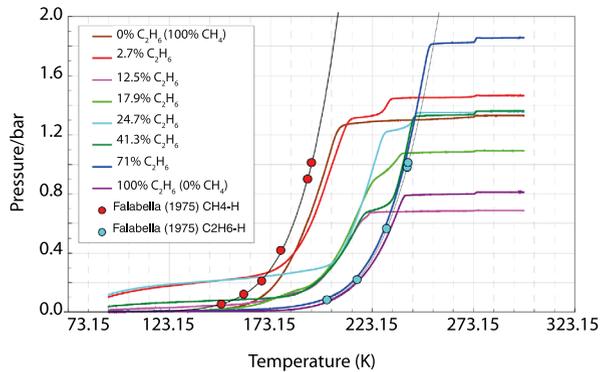
Fig. 4 Equilibrium curves of clathrates (*horizontal lines*) together with an evolutionary track of the protosolar nebula at the heliocentric distance of 5 AU (adapted from Mousis and Alibert 2006). This evolutionary track corresponds to the thermodynamic pathway followed by the disk during its cooling at the considered distance (the evolution of the disk proceeds from high to low temperatures). Abundances of various elements are solar



observed in comets and in ISM (Gibb et al. 2000, 2004; Bockelée-Morvan et al. 2004; van Dishoeck 2004; Mumma and Charnley 2011). The equilibria of single guest clathrates of CH_4 , CO_2 , H_2S , Xe and Kr are fairly well constrained at low temperature (mainly in the 150–270 K range) and low pressure (> 1 mbar most of the time; see data in Fray et al. 2010; Marboeuf et al. 2012a, and Mohammadi and Richon 2013). However, for the highly volatile species CO, N_2 , and Ar, the experimental data are very scarce and mainly at high temperature (> 260 K) (Holder et al. 1980; Mohammadi and Anderson 2010, 2011), expected for the single guest clathrate of Ar for which data exist below 150 K (Barrer and Edge 1967). Meanwhile, as discussed in Fray et al. (2010) and Marboeuf et al. (2012a), experimental data for Xe and Kr clathrates from Barrer and Edge (1967) present a progressive deviation compared to other measurements, indicating that their data are not reliable. Hence, clathrates of highly volatile species CO, N_2 and Ar are not well constrained in thermodynamic conditions close to those met in comets and in the protosolar nebula (see Fig. 4). Yet, such data are very important to understand the fractionation of these species during the formation and evolution of ices in the protosolar nebula (Iro et al. 2003; Mousis et al. 2009b, 2012a, 2012b, 2014), comets, icy moons and dwarf and terrestrial planets (Marboeuf et al. 2012b; Mousis et al. 2002, 2009a, 2011, 2013a, 2013b; Thomas et al. 2007, 2008). It is important to note that no experimental data concerning the stability curve of the CH_3OH clathrate has been reported in the literature and the conditions under which it forms stoichiometric hydrates or clathrate (Blake et al. 1991; Notesco and Bar-Nun 2000) are still unclear. Moreover, NH_3 is known to form rather stoichiometric hemihydrates ($2\text{NH}_3\text{-H}_2\text{O}$) and/or monohydrates ($\text{NH}_3\text{-H}_2\text{O}$) under low-pressure conditions (Lewis 1972; Bertie and Refaat Shehata 1984; Lunine and Stevenson 1987; Moore et al. 2007). This molecule has also been assigned a role of anti-freeze for water ice and clathrate formation, modifying the stability region of the solid ice and methane clathrate hydrate phases as a thermodynamic inhibitor (Choukroun et al. 2006, 2010; Fortes and Choukroun 2010; Shin et al. 2012). However, one study has shown that ammonia can form clathrates and participate synergistically in the formation of the cages in the presence of methane gas at low temperature (Shin et al. 2012), but the conditions under which clathrates are formed remain unclear and no experimental data allowing us to determine the conditions of formation of the NH_3 clathrate has been reported in the literature.

Of particular interest is the fractionation of volatile species during the formation of clathrates in presence of a gas mixture composed of several different volatile molecules. The presence of several volatile species in the gas phase can generate the formation of a multiple

Fig. 5 Equilibrium pressure of $\text{CH}_4 + \text{C}_2\text{H}_6$ hydrate for several different abundances of species in the gas phase (adapted from Hachikubo et al. 2008)



guest clathrate whose equilibrium pressure varies as a function of the gas phase composition and the temperature (see Fig. 5). The trapping efficiencies of gases in clathrate in equilibrium with a gas mixture are very scarce. They are currently limited for temperatures greater than 200 K (Kang et al. 2001; Rydzy et al. 2007; Hachikubo et al. 2007, 2008), for a very small number of dataset, and for molecules which are not necessarily of great interest in planetary science ($\text{C}_3\text{H}_8 + \text{Ar}$, $\text{C}_2\text{H}_6 + \text{Ar}$, $\text{CO}_2 + \text{N}_2$, $\text{CO}_2 + \text{N}_2 + \text{C}_4\text{H}_8\text{O}$, $\text{CH}_4 + \text{CO}_2$, $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$). No other experimental data, to our current knowledge, give the fractionation of volatile molecules in clathrates in equilibrium with a gas mixture at lower temperature (<200 K). Other studies giving the equilibrium pressure of multiple guest clathrates exist for different dataset and volatile species, but these studies do not give the abundance of volatile species both in the gas phase and in clathrate, and are limited most of the time to temperatures close to 270 K or above the triple point (Maekawa 2001; Linga et al. 2007; Mohammadi and Anderson 2009; Yasuda et al. 2010). Yet, both informations on the mole fractions of species in the clathrate structure and in the surrounding gas phase are needed to characterize the fractionation process during volatile trapping. In particular, the investigation of the composition of clathrates formed from gas mixtures of $\text{CO} + \text{N}_2$, $\text{CO} + \text{CO}_2$, $\text{CO} + \text{CH}_4$, and mixtures of noble gas ($\text{Xe} + \text{Kr}$, $\text{Xe} + \text{Ar}$, $\text{Kr} + \text{Ar}$, and $\text{Xe} + \text{Kr} + \text{Ar}$) are fundamental for studies of comets. While H_2O is the predominant molecule and least volatile other than the refractory larger organics, CO is the most abundant volatile specie in comets, and CO_2 and CH_4 the two other abundant carbon-bearing species (Bockelée-Morvan et al. 2004). N_2 is currently not observed in comets and it could not be trapped in the clathrate structure, explaining its apparent under-abundance in comets (Iro et al. 2003; Mousis et al. 2012a). The presence of noble gases in comets is still under debate.

Of great interest is also the fractionation of isotopic ratios between gas and clathrates. Isotopic ratios measurements are the classical methods for investigating the origin of solar system materials. But these measurements are very scarce in clathrates. Only a few data on the isotopic fractionation of carbon in molecules C_2H_6 and CH_4 have been obtained, but for temperatures greater than 250 K (Hachikubo et al. 2007).

Another issue remains the kinetics of formation and dissociation of clathrates from/to pure crystalline water ice and gas interaction. Two main stages of the clathrate formation process are distinguished (Kuhs et al. 2006). The first stage, relatively rapid, corresponds to the formation of a clathrate film over the pure crystalline ice surface (stage I), and the second, which dominates when the whole ice grain is covered by a clathrate layer, is the growth of the shell of clathrate phase around ice grains (stage II), with gas and water mass transports (diffusion) through the clathrate layer. For the first stage, a few kinetics experimental

data have been determined only for pure clathrates of CH₄ and CO₂, mainly in the 185–270 K range (Schmitt et al. 1989; Staykova et al. 2003; Wang et al. 2002; Kuhs et al. 2006; Falenty et al. 2011). The authors have assumed that the value of the kinetics parameter of formation/dissociation of clathrates follows an Arrhenius-type function of temperature. However, the physical parameters that may affect the value of kinetics are multiple: temperature, activity of the ice surface (mobility of water molecules), type of gas molecule, thickness of clathrate formed, thermal history, etc. The kinetics conditions of the formation of the clathrate structure from pure crystalline water ice and gas species are currently poorly constrained at low temperature and the kinetic feasibility of the formation of clathrates in the cooling disk or in icy objects is still under debate, even if appropriate thermodynamics conditions are encountered for clathrate formation (Marboeuf et al. 2012b, 2014, Marboeuf and Schmitt 2014, Mousis et al. 2008, 2009a, 2009b, 2012a, 2014).

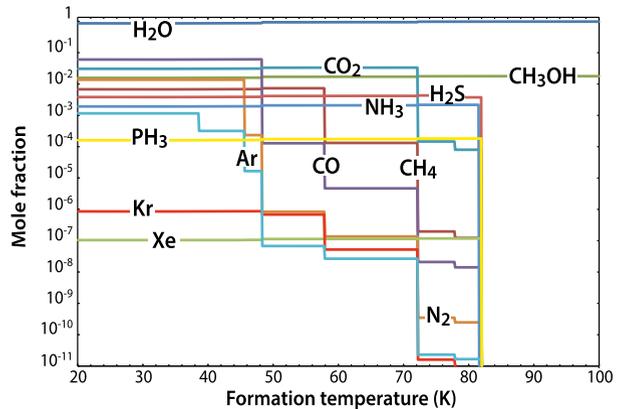
3.2.2 Prediction of Clathrates Composition from Thermodynamic Models

Because of the scarcity of experimental data at thermodynamic conditions representative of those encountered in the protosolar nebula, pressure-temperature equilibrium curves are usually extrapolated via the fit of existing data down to ~ 20 K (Gautier et al. 2001; Hersant et al. 2004, 2008; Mousis et al. 2009b, 2012a). For example, the equilibrium curve of N₂ clathrate is experimentally known at pressures higher than ~ 60 bars (Lunine and Stevenson 1985), implying that it has to be extrapolated over more than 13 orders of pressure magnitudes (given that solar N₂/H₂ is $\sim 10^{-5}$; Lodders et al. 2009) to derive its formation temperature at nebular conditions. The case of CO is very similar since its equilibrium curve is derived from experimental data obtained at pressures above 135 bars (Mohammadi et al. 2005). The extrapolated equilibrium curves are used to infer the temperature and pressure corresponding to the formation conditions of clathrates in the protosolar nebula via the use of protoplanetary disks models (see Fig. 4).

These calculations allow providing estimates of the composition of icy planetesimals condensed in the protosolar nebula (Marboeuf et al. 2008; Mousis et al. 2008) but their reliability depends upon the quality of the fits of the experimental data, which remain unconstrained given their large deficiency at low-pressure conditions. One also has to mention that the kinetics of clathrate formation is not considered in these calculations, due again to the absence of experimental data at low-pressure range. Kinetics is an important factor because a low formation rate would impede the agglomeration of large amounts of clathrates in the building blocks of icy bodies of the outer solar system. On the other hand, turbulent mixing in the protosolar nebula may ease the formation of clathrates since the collision between grains would expose fresh surfaces of ice to the gas and then favor its entrapment. In any case, because the question of clathrate formation kinetics in the protosolar nebula remains open, all existing models assume equilibrium formation conditions. Another restriction of the clathration efficiency in the protosolar nebula is the availability of crystalline water, which usually condenses at ~ 150 K. A full clathration of volatiles present in the gas phase of the protosolar nebula requires that the abundance of crystalline water is ~ 2 times higher than that of protosolar oxygen (Gautier et al. 2001; Mousis et al. 2014). If the water abundance is assumed to be protosolar, then a significant fraction of volatiles cannot be trapped in clathrates (Mousis et al. 2009b) and forms pure condensate at lower temperature in the 20–30 K range if the nebula effectively cooled down to these temperatures.

When the amount of available water is lower than the one required for the full clathration of the volatiles present in the gas phase, it is preferable to use of a statistical

Fig. 6 Composition of the volatile phase incorporated in planetesimals formed beyond the snow line in the protosolar nebula as a function of their formation temperature (adapted from Mousis et al. 2014). The water abundance is assumed to be sufficiently high to allow full trapping of volatiles in the clathrate phase. Computations have been made with a statistical model derived from the approach of Van der Waal and Platteeuw (1959)



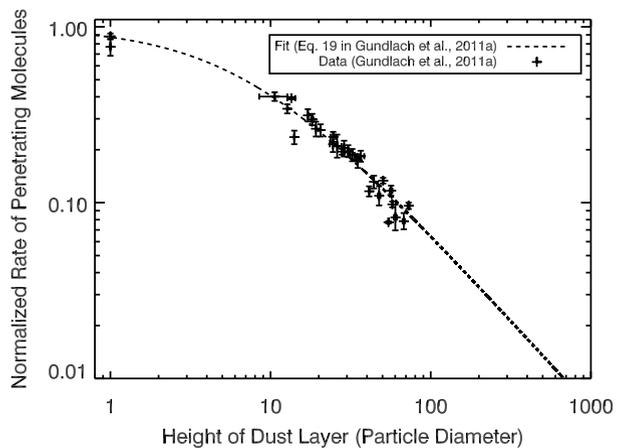
thermodynamic model (Van der Waal and Platteeuw 1959; Parrish and Prausnitz 1972; Lunine and Stevenson 1985; Thomas et al. 2007, 2008; Mousis et al. 2013a, 2013b) for the computation of the planetesimals composition because the different molecules do not have the same propensities for trapping. Statistical thermodynamic models are based on a very simple expression of the interaction energy between the guest and the surrounding water molecules. These models are commonly used in industry and science because they save substantial experimental effort for the determination of (i) the equilibrium pressure of a clathrate formed from various mixtures; and (ii) the mole fraction of the different species trapped in clathrate from a given gas or liquid phase. Their accuracy depends on the reliability of the parameters used to calculate the water-molecules interactions and also on the type of molecules considered. These models are fairly well constrained near the triple point of ice but their validity remains unverified in the 100–200 K temperature range because there is no experimental data against which the individual interaction potential can be fitted. Figure 6 represents the composition of planetesimals agglomerated from clathrates formed in the outer part of the protosolar nebula and calculated from a statistical thermodynamic approach (Mousis et al. 2014). It shows that all species under consideration can be trapped in clathrates at temperatures as high as ~80 K in the nebula but with very different mole fractions. The mole fractions of volatiles trapped in clathrates vary as a function of the disk's temperature. The final composition of planetesimals will depend on the temperature at which the protosolar nebula has cooled down before its dissipation.

4 Comet Surface

4.1 Thermal Properties of Cometary Surfaces

Laboratory experiments were carried out in order to investigate the heat and mass transfer in cometary surface layers (Gundlach et al. 2011a; Gundlach and Blum 2012). Therefore, an experimental setup was constructed to measure the gas production rate and the heat conductivity of cylindrical cometary analogue samples (diameter: 2.5 cm; typical height: 3 cm) at low pressures ($< 10^{-5}$ mbar) and low temperatures (between 120 K and 300 K). The cometary analogue samples were composed of hexagonal water ice (produced in a freezer) covered by a dust layer, which was composed of SiO₂ grains with different radii ($20 \pm 8 \mu\text{m}$, $89 \pm 30 \mu\text{m}$, $186 \pm 63 \mu\text{m}$, $254 \pm 42 \mu\text{m}$ and $463 \pm 32 \mu\text{m}$). The outgassing rate of the water

Fig. 7 Normalized rate of penetrating molecules through a dust layer with respect to the height of the dust layer (adapted from Fig. 8 in Gundlach et al. 2011a). The data (plusses) are obtained by covering a sublimating ice surface by dust layers with variable thickness and a volume filling factor of 0.59. The *dashed curve* shows the fit to the data, which is motivated by the fact that the dust layer acts like a resistor to the gas flux (Eq. 19 in Gundlach et al. 2011a)



ice through the dust layer was measured for different temperatures of the water ice surface and for different heights of the covering dust layer. These experiments showed that the presence of a dust layer could sufficiently decrease the outgassing rate of water ice in vacuum (see Fig. 7). For dust layers possessing thicknesses larger than approximately ten particle diameters, the outgassing rate is inversely proportional to the thickness of the covering dust layer. This behavior can be explained by the idea that the dust layer acts like a resistor to the gas flux.

Additionally, the experimental setup was used systematically to determine the temperature dependency of the so-called sublimation coefficient (temperature range: ~ 160 K to ~ 220 K), introduced by Kossacki et al. (1999). This coefficient describes the deviation of the sublimation rate measured in the laboratory from the sublimation rate calculated by the Hertz-Knudsen formula (see Eqs. 2 and 3 in Gundlach et al. 2011a). These experiments revealed that the sublimation coefficient is unity at temperatures below ~ 194 K (see Eq. 20 in Gundlach et al. 2011a) and decreases steeply (over a temperature range of ~ 20 K) to a value of 0.15 at higher temperatures. This implies that the Hertz-Knudsen formula overestimates the gas production rate of water ice by approximately one order of magnitude at temperatures above ~ 194 K.

Thermal conductivity of the surface layer of a comet is an important physical parameter that needs to be constrained. While this is a mix of dust, organics, and ice, all these may play a critical role. Thermal conductivity of comets is known to be very low, e.g., $\sim 1 \times 10^{-3} \text{ WK}^{-1} \text{ m}^{-1}$ (Groussin et al. 2007) in the case of 9P/Tempel 1, estimated from thermal inertia measurements ($50 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-0.5}$). Unfortunately, the thermal inertia estimation strongly depends on the surface roughness (Davidsson et al. 2013), which is not well known in the case of Tempel 1. Heat conductivity of porous, amorphous ice is reported to be $3 \times 10^{-2} \text{ WK}^{-1} \text{ m}^{-1}$ (Bar-Nun and Laufer 2003), which is larger than that of comet Tempel 1. In the laboratory (KOSI experiments), the heat conductivity of porous cometary analogue materials, composed of different non-volatile and volatile materials, was measured to be much higher at $\sim 3 \times 10^{-1} \text{ W/Km}$ (Spohn and Benkhoff 1990). This value is lower than the bulk heat conductivity of water ice but much higher than the heat conductivity estimated for the surface material of Tempel 1.

The heat conductivity of dust layers in vacuum was measured by using the same experimental setup (Gundlach and Blum 2012). Therefore, dust layers of different heights were illuminated by an external light source with intensities ranging from 0.3 to 5.3 Solar con-

starts. During these experiments, the bottom and the surface temperature of the dust layers were continuously measured by a temperature sensor and an infrared camera, respectively. The temperature data were then used to compute the heat conductivity of the samples, which depends on the particle size (between 40 μm and 1 mm) and on the temperature of the dust layers. These measurements showed that the heat conductivity of dust layers in vacuum is relatively low (between $10^{-1} \text{ W m}^{-1} \text{ K}^{-1}$ and $10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$; see Figs. 10 and 11 in Gundlach and Blum 2012), and that the heat is transported by different mechanisms: (1) by heat conduction through the solid network of particles and (2) by radiation within the pores of the dust layers. The heat flow through the solid network of particles dominates for small particle sizes and at low temperatures (e.g., for particle sizes smaller than $\sim 15 \mu\text{m}$ and for temperatures below $\sim 300 \text{ K}$). In this case, the heat conductivity of the bulk material determines the temperature dependency of the heat conductivity of the dust layer. With increasing particle radius, R , the heat conductivity decreases as $\lambda \sim R^{-1/3}$, where λ is the heat conductivity of the dust layer (see Eq. 12 in Gundlach and Blum 2012). The heat transport is dominated by radiation, if the dust layers are composed of larger particles, or at higher temperatures (e.g., for particle sizes larger than $\sim 15 \mu\text{m}$ and temperatures above $\sim 300 \text{ K}$). In this case, the heat conductivity strongly depends on temperature ($\lambda \sim T^3$, where T is the temperature of the dust layer) and increases linearly with increasing particle radius ($\lambda \sim R$; see Eqs. 5 and 13 in Gundlach and Blum 2012).

Additionally, the heat conductivity of aggregate layers (dust layers composed of aggregates, which consist of micrometer-sized particles; see Fig. 13 in Gundlach and Blum 2012) was measured by Krause et al. (2011). The heat conductivity of aggregate layers is approximately an order of magnitude lower (between $10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$ and $10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$; see their Fig. 2) than the heat conductivity of dust layers composed of single solid particles. However, radiation can be an important heat transport mechanism in the case of aggregate layers, which can effectively increase the heat conductivity (for aggregate sizes larger than $\sim 0.1 \text{ mm}$; see Fig. 8). For example, an aggregate layer consisting of 1 cm-sized aggregates at a temperature of 300 K possess a heat conductivity of $1 \times 10^{-1} \text{ W m}^{-1} \text{ K}^{-1}$, which is approximately two orders of magnitude higher than the heat conductivity without radiative heat transport.

If cometary surface layers are composed of aggregates, the strong temperature dependency of the radiative heat transport ($\lambda \sim T^3$) implies diurnal variations of the heat conductivity on the order of one to three orders of magnitude. Thus, future measurements should aim at investigating the diurnal variations of the heat conductivity (or, the thermal inertia) of cometary surface materials in order to derive the structure (i.e., aggregate size and volume filling factor) of the surface material.

Further experiments were carried out in order to investigate the tensile strength of the cometary surface material (Blum et al. 2014). Therefore, dust aggregates of two different sizes ($0.66 \pm 0.14 \text{ mm}$ and $1.29 \pm 0.29 \text{ mm}$) were poured carefully onto a grating inside a glass tube to form aggregate layers with several centimeters in height. With the help of a vacuum pump, different pressure gradients were applied to the aggregate layers until a break-up of the samples was observed. From the pressure difference at the moment of the breakup, the tensile strength of the aggregate layers was derived and yielded $1.3 \pm 0.9 \text{ Pa}$ in the case of the 0.66 mm-sized aggregates and $0.8 \pm 0.7 \text{ Pa}$ in the case of the 1.29 mm-sized aggregates, respectively. This ultra-low tensile strength is in a good agreement with model calculations, which predict a decreasing tensile strength with increasing aggregate size (see Skorov and Blum 2012, for details).

In addition to the laboratory investigations mentioned previously, μm -sized water-ice particles were produced and used in the laboratory in order to generate a more realistic cometary

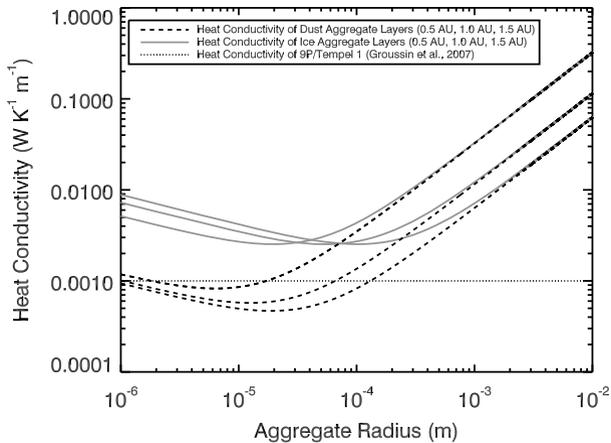


Fig. 8 Heat conductivity of aggregate layers with different aggregate sizes covering a comet nucleus. The heat conductivity of the aggregate layers is derived by the heat conductivity model developed by Gundlach and Blum (2012). The calculations were performed for ice aggregates (*gray, solid curves*) and for dust aggregates (*black, solid curves*) with a Bond albedo of 0.04 and at different heliocentric distances: 0.5 AU, 1.0 AU and 1.5 AU (from *left to right*, respectively). This model is capable to predict the heat conductivity for aggregate size smaller than the diurnal skin depth, which is typically in the cm-range. Additionally, the heat conductivity of the surface material of Comet 9P/Tempel 1 (Groussin et al. 2007) is shown by the dotted line. Here, we would like to remind the reader that the heat conductivity of the surface material is derived from the thermal inertia estimation, which strongly depends on the surface roughness of the nucleus

analog material (Gundlach et al. 2011b). The μm -sized water-ice particles were produced by spraying with an inhalator directly into liquid nitrogen, or into a cold ($T < 200\text{ K}$) sedimentation chamber. The particles produced by these two methods are visibly spherical (see Fig. 3 in Jost et al. 2013) and possess a mean radius of $1.47^{+0.96}_{-0.58}\ \mu\text{m}$, with particle radii ranging from $\sim 0.2\ \mu\text{m}$ to $\sim 7\ \mu\text{m}$ (Jost et al. 2013).

First experiments with this novel sample material revealed a relatively high surface energy of water ice ($0.19\ \text{J m}^{-2}$; Gundlach et al. 2011b) in comparison to silica particles ($0.02\ \text{J m}^{-2}$; Poppe et al. 2000), which implies that water-ice particles can stick at higher collision velocities than silica particles. The specific surface energy of the μm -sized water ice particles was measured by observing the gravitational restructuring of ice aggregates composed of μm -sized water-ice particles with a long-distance microscope (Gundlach et al. 2011b).

Furthermore, the μm -sized water-ice particles, produced by spraying the water droplets into the cold sedimentation chamber, were used to measure their sticking threshold (the velocity until the particles stick in collisions; Gundlach and Blum 2015). Therefore, the μm -sized water-ice particles were extracted by a vacuum system from the cold sedimentation chamber into a vacuum chamber. Inside the vacuum chamber, the μm -sized water-ice particles formed an ice-particle jet, and collided with a cryogenically cooled target. These experiments showed that the sticking threshold of the μm -sized water-ice particles is at $\sim 10\ \text{m s}^{-1}$, which is approximately ten times higher than the sticking threshold estimated for micrometer-sized silica particles ($\sim 1\ \text{m s}^{-1}$; Poppe et al. 2000).

In conclusion, experimental studies presented in this section aim at supporting models on cometary activity and to help preparing future comet sample-return mission. So far, experiments have been focused on investigating outgassing properties of water ice under cometary conditions (i.e., illuminated, at low temperatures, under low pressure, and covered by dust

layers), which have shown that dust layers have a major influence on the water ice activity. Our studies (Gundlach et al. 2011a) confirmed the unexpected behavior of water ice to decrease its activity around ~ 200 K by almost one order of magnitude, proposed by Kos-sacki et al. (1999). It was found that porosity of the material has a strong influence on the effective heat conductivity (Gundlach and Blum 2012). Cometary surface material has been simulated by layers composed of dust aggregates (which themselves consist of micrometer-sized dust particles) and we found that these dust aggregate layers possess ultra-low tensile strength (Blum et al. 2014), confirming earlier predictions by Skorov and Blum (2012). Using micrometer-sized water ice particles, it was shown that water ice particles can stick at velocities up to ~ 10 m s⁻¹ (Gundlach and Blum 2015), which is approximately one order of magnitude higher compared to the sticking threshold velocity of micrometer-sized silica particles at 1.2 m s⁻¹ (Poppe et al. 2000). Further studies are needed to determine the tensile properties of organic dust, crystalline and amorphous ice aggregates, and differences in the physical properties of volatiles trapped in crystalline and amorphous ices, including clathrates.

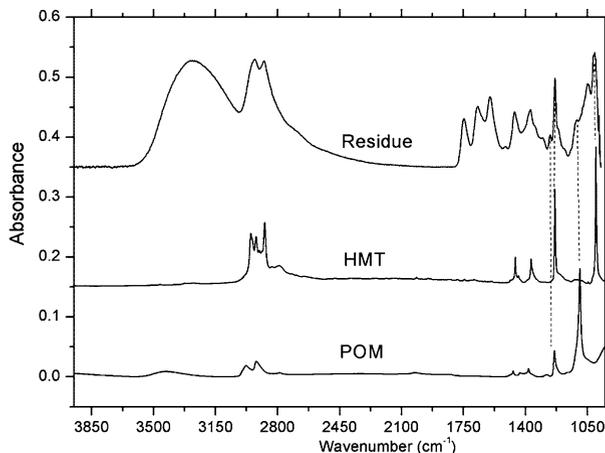
4.2 Refractive Organic Matter on Comets—Laboratory Studies

Many experimental devices have been developed to investigate the formation of organic molecules in cometary environments. In the laboratory, irradiation by UV photons or charged particles followed by thermal heating of astrophysical ice analogues that contain simple molecules such as H₂O, CH₃OH, NH₃ and CO₂ have produced a suite of complex organic molecules similar to those found in small bodies of our Solar system, including amino acids and nucleobases (Gerakines et al. 1996; Muñoz-Caro et al. 2002; Bernstein et al. 1995, 2002). When UV photons are penetrating into astrophysical ices, they break bonds, producing radicals and activated species. It has recently been shown by Gudipati and coworkers (Gudipati and Yang 2012; Henderson and Gudipati 2014; Yang and Gudipati 2014) that even at very low temperatures (5 K) UV-irradiation of water-ice containing organics (PAHs) lead to hydrogenation and oxygenation/hydroxylation. While these primary chemical processes between organic radicals/ions with radicals and ions produced from water matrix (H, OH, O, etc.), UV-irradiation by itself may not produce large complex organic compounds. When the irradiated ices are subjected to annealing to higher temperatures the photoproducts become mobile and could react more readily forming a non-volatile complex organic residue. During this warming, a large part of volatile compounds desorb with the most abundant molecule, water. The characterization of these volatile species is important, since they certainly take a part in the subsequent formation of this refractory residue. Here, the refractory organic residue refers to all compounds having a higher temperature desorption than that of water, which is the most abundant molecule of a cometary ice analogue.

4.2.1 Characterization of the Whole Residues

As already described, after the sublimation of volatile organic compounds (VOC), a residue is present at the surface of sample holders. These residues are supposed to be the first step toward organic matter found in comets, asteroids or meteorites. That is why they are considered as potential analogues of cometary organic matter. Different analytical methods have been tested to determine the molecular constitution of such residues and have shown important concordance between these analogues and the soluble organic matter of meteorites.

Fig. 9 Infrared spectrum of an organic residue obtained after UV photolysis (9 h) and warming at 300 K of an ice mixture with $\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3$ composition compared with infrared spectra of pure HMT recorded at 300 K and pure POM recorded at 300 K. The residue was produced by Pierre de Marcellus using the MICMOC experiment at IAS, France (Danger et al. 2013)



A method usually used for characterizing these residues is the infrared spectroscopy, because it provides an in situ residue analysis without sample degradation, and a direct comparison to observational data. Infrared spectra of these residues have shown the presence of polar compounds such as amines, carboxylic acid or amides functions (Allamandola et al. 1988; Bernstein et al. 1995; Muñoz-Caro and Schutte 2003). Some specific compounds have also been identified, such as the hexamethylenetetramine (HMT), which seems to represent a large part of the organics constituting these residues. In addition to these compounds, some polymers have been characterized, such as the polyoxymethylene (POM) as shown in Fig. 9. Infrared spectroscopy was also used for estimating the impact of the source of energetic processes applied to the ice before its warming. It was shown that infrared spectroscopy of residue spectra presenting rather similar characteristics are obtained between an ice initially irradiated by VUV photons or by ions (Islam et al. 2014; Muñoz-Caro et al. 2014), even if some abundance variations can be observed. However, if infrared spectroscopy can give first clues on the most abundant molecules present in such residues as well as on their formation mechanisms (see Sect. 4.3), a drawback of this analytical method is its low sensitivity and the difficulties to obtain a clear identification of molecular species in a complex mixture due to the overlapping of broad solid-state bands. Consequently, numerous other analytical techniques have been used for determining the molecular constitution of these residues.

Mass spectrometry is another analytical method that can provide the characterization of the entire residue without the need of sample derivatization or degradation. Laser desorption mass spectrometry was used to identify polyaromatic hydrocarbons (PAH) (Dworkin et al. 2004; Spencer et al. 2008). Nevertheless, depending on the resolution used, mass spectrometry cannot be sufficient for the analysis of the molecular complexity present in refractory residues. New mass spectrometry systems presenting high resolution mass spectrometry (HRMS) such as FT-ICR (Fourier Transform Ion Cyclotron Resonance) or orbitrap, present enough resolution for that sort of characterization. These techniques were used for the analysis of the Murchison meteorite (Schmitt-kopplin et al. 2010) and the analysis of biomolecules coming from the hydrolysis of tholins (Neish et al. 2010). Recently, the orbitrap was used for the analysis of residues formed by the VUV irradiation and the warming of ice analogues containing $\text{CH}_3\text{OH} : \text{NH}_3 : \text{H}_2\text{O}$ with $^{12}\text{CH}_3\text{OH}$ or $^{13}\text{CH}_3\text{OH}$ (Danger et al. 2013). In the protocol used, residues are dissolved in methanol and directly injected in the orbitrap without any degradation. Molecules are ionized through an electrospray source (ESI),

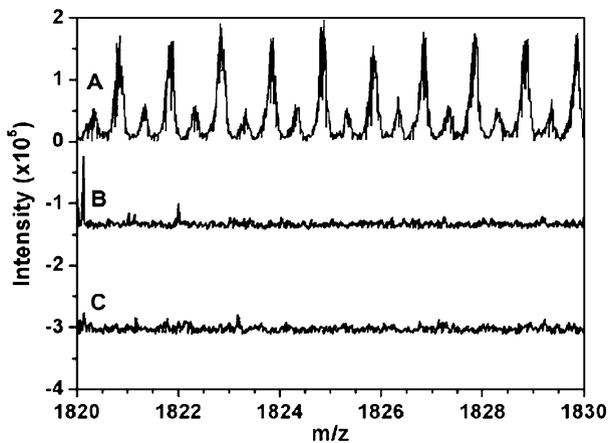


Fig. 10 FT-orbitrap SIM spectra obtained in ESI negative mode for the m/z range 1820–1830 after recovery in methanol of (A) a refractory residue formed from an ice mixture containing $^{12}\text{CH}_3\text{OH} : \text{NH}_3 : \text{H}_2\text{O}$ (1:1:3), (B) a blank coming from an ice mixture deposited on the MgF_2 window and warmed without VUV irradiation, and (C) a blank coming from a VUV irradiation of the MgF_2 window, without gas mixture deposit. Between blanks and sample formation, all the different steps are exactly the same. Reprinted from Danger et al. (2013) with permission from Elsevier

which provides smooth molecule ionization and the molecular ion detection. The mass spectra present an intensity that progressively decreases when m/z increases. Furthermore, the HRMS provides a zoom in this distribution, which emphasizes the diversity of molecules constituting this refractory residue. While the started ice is only composed of three simple molecules H_2O , CH_3OH and NH_3 , HRMS analyses have shown that more than ten of thousand of ions (i.e. structures) are detected with masses up to 4.000 Da. These results confirmed a previous report of the high m/z ratios up to 2600 detected by MALDI-TOF technique in similar organic residues (Modica et al. 2013). An example of a mass spectrum obtained with orbitrap in negative ESI mode is displayed in Fig. 10A into the range m/z 1820 to 1830 for a residue analysis coming from an ice containing $^{12}\text{CH}_3\text{OH} : \text{NH}_3 : \text{H}_2\text{O}$ in ratio 1:1:3. If this profile is compared to two different blanks (Fig. 10 traces B and C), ions are only detected in the residue, confirming that molecular species detected come from the photochemistry and the warming of the initial ice. Therefore, the composition of residues is extremely rich and complex. It has to be noted that a warming alone cannot lead to the molecular diversity observed (Fig. 10B). This molecular diversity is only obtained if VUV irradiations are associated with a warming. This reactivity aspect will be further discussed in Sect. 4.3. Furthermore, next to this global residue analysis, the HRMS can also provide in a same run the analysis of specific molecules. HRMS has for example confirmed the presence of HMT already observed by infrared spectroscopy in such residues. Finally, this whole residue analysis has allowed obtaining an estimation of the residue elemental composition.

4.2.2 Search for Specific Molecules in Residues

Even if HRMS analyses can provide in some cases the search for specific molecules, more accurate analytical techniques are used for this aim. GC-MS or LC-MS were extensively used. They provide the identification of various amino acids (Bernstein et al. 2002; Muñoz-Caro et al. 2002). Interestingly, amino acids are detected before residue hydrolysis, their

yield increasing after hydrolysis (Meinert et al. 2012). These results suggest different amino acid formation coming from different pathways (Elsila et al. 2007; Danger et al. 2011a; Danger et al. 2011b; Bossa et al. 2010). GCxGC-MS has provided the identification of 30 amino acids (Meinert et al. 2012). Even if the initial ices are different as well as the physical source of energy (photons, electron or ions) applied to these ices, in each case amino acids are detected. Interesting experiments using VUV circularly polarized light instead of a linearly polarized light commonly used, have shown that enantiomeric excess up to 2.54 % in the L form can be obtained on amino acids by this process, the sign of these enantiomeric excesses depending on the helicity and the energy of the CPL (de Marcellus et al. 2011b; Modica et al. 2014). The use of UV-CPL is a scenario that could explain the detection of enantiomeric excess in some meteorites. The enantiomeric excess formed by this process could then be enhanced in parent bodies of meteorites. Other analyses also made without a preliminary residue hydrolysis provide the identification of various linear or cyclic compounds containing nitrogen and/or oxygen chemical functions (Meierhenrich et al. 2005; Nuevo et al. 2010; de Marcellus et al. 2011a; Materese et al. 2014), such as urea, hydantoin, glycolic acid, glycerol or hexahydro-1, 3, 5-triazine (TMT). All these molecules are considered as possible sources of matter for the development of a prebiotic chemistry in a specific environment (Danger and Le Sergeant d'Hendecourt 2012). Other analyses provide the confirmation of the HMT presence; the influence of the initial ice mixture composition on its formation being investigated using GC-MS (Cottin et al. 2001; Muñoz-Caro et al. 2004). HPLC analyses also provide the detection of amphiphilic molecules (Dworkin et al. 2001). Some ices were doped with pyridine derivatives and their analyses have shown the presence of nucleic bases such as uracil, cytosine and thymine (Nuevo et al. 2012; Nuevo et al. 2014).

Residue characterizations show an important molecular diversity (Danger et al. 2013). Interesting similarity can be found between these residues and the soluble organic matter (SOM) of meteorites. The whole characterization described a similar molecular diversity, and specific analyses demonstrate the presence of common compounds. Even if these residues cannot be considered as the SOM of astrophysical objects, they can be considered as analogues of the first step that will then lead to the SOM formation.

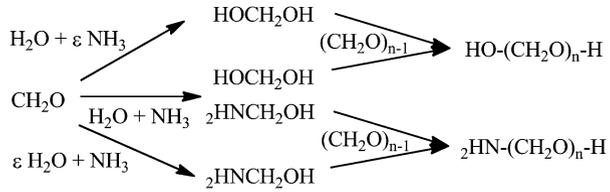
These analyses also demonstrate a necessity of an energetic process at the beginning of the ice deposit. If this energetic process is not present no reactivity or only a low reactivity occurs depending on the initial ice composition. However, the reactivity leading to refractory residues is much more complex than an only VUV irradiation or ion bombardment. The ice heating after irradiation or bombardment is an essential process that will then lead to the residue formation (Theule et al. 2013). As it will be discussed in the next section, physical processes (VUV irradiations or ion bombardment) have to be associated to a thermal reactivity for explaining the molecular diversity observed. Based on these observations, we can thus propose that the organic matter detected in interplanetary objects comes from the association of high energetic processes and thermal heating.

4.3 Precursors for Refractory Organics

4.3.1 Water Ice Impact on Chemical Reactivity

In cometary environments, water is the most abundant molecule. As for desorption of volatiles, water will play an important role in the chemical composition (Martin-Domenech et al. 2014) and reactivity (Jenniskens and Blake 1994). Indeed, at low temperature, the chemical reactivity is dominated by the kinetics of diffusion of the molecules in the

Fig. 11 Formaldehyde (CH_2O) reactivity in ices containing various $\text{H}_2\text{O}/\text{NH}_3$ ratios



amorphous solid water (ASW, also known as amorphous ice). Barrier-less reactions involving photo-produced radicals (Schutte 1995) or low-barrier reactions involving neutrals (Theule et al. 2013) are strongly limited by the ability of reactants to diffuse and meet each other. The diffusion-limited reactivity mechanisms are poorly known. The diffusion of species in the ice is itself poorly known. While bulk and surface diffusion coefficients have been measured in crystalline ice (Livingston et al. 2002; Varotsos and Zellner 2010), little measurements exist for diffusion in ASW (Mispelaer et al. 2013; Daschbach et al. 2004). Measuring reliable diffusion coefficients in water ice at low-temperature is a current challenge. Diffusion of volatiles in ASW seems to be related to the water ice substrate crystallization (Mispelaer et al. 2013). Understanding the implication of this seemingly crystallization-driven diffusion on reactivity is central to quantify the kinetics of complex organic matter formation in ice.

However, a water environment have others impacts on reactivity than diffusion. Experiments have shown that water can act as a catalyst for the formation of complex organic molecules. For instance, the formation of POM initiated by HCN ($\text{NC}-(\text{CH}_2-\text{O})\text{-H}$) can only occur in presence of water, since water dissociates HCN forming $\text{}^-\text{CN}$ that can then react on H_2CO (Danger et al. 2014). Furthermore, as discussed previously, molecules are trapped in the water matrix during the ice formation on grains. This trapping also plays a fundamental role in reactivity. A study on the reactivity between acetone $(\text{CH}_3)_2\text{CO}$ and ammonia NH_3 at low temperature and low pressure (20–300 K, 10^{-9} mbar) for the formation of $\text{}_2\text{HN-C}(\text{CH}_3)_2\text{-OH}$, an amino acid precursor, have shown that without water, the reaction does not occur, because reactants desorb before reacting (Fresneau et al. 2014). However, when acetone/ NH_3 is mixed with a water ice, reactants are trapped in the water matrix up to the water desorption temperature, at which sufficient energy is available for acetone and NH_3 to react before their desorption. These examples demonstrate that the role of water in reactivity is fundamental for the formation of complex molecules in cometary environment. We also note that HCN polymers are also proposed to exist on comets and contribute to the potential prebiotic molecules that could have lead to the origin of life on Earth (Matthews and Minard 2006).

4.3.2 Formaldehyde Chemistry in Cometary Ices: POM Formation

The presence of POM ($\text{HO}-(\text{CH}_2\text{O})\text{-H}$) on grains of the comet 1P/Halley was first claimed in 1987 by Huebner (Huebner 1987), because mass spectra recorded by the PICCA instrument on the *Giotto* mission showed a regular pattern of peaks consistent with a POM-like structure. However, it was shown afterward that this regular pattern can also be due to the presence of complex molecules containing C, H, O and N atoms, including POM-like structures (Mitchell et al. 1992). Although the presence of POM in comets has not yet been confirmed, some experimental results support its presence in cometary grains. POM and POM-like polymers can indeed be formed from the heating of interstellar/cometary ice analogues (Schutte et al. 1993a, 1993b; Danger et al. 2012, 2014; Duvernay et al. 2014a;

Noble et al. 2012). POM has also been detected in laboratory analogues of interstellar/cometary grains by the thermal processing of ices containing H_2O , H_2CO and NH_3 (Vinogradoff et al. 2011). Thermally induced formaldehyde reactions at low temperature in $\text{H}_2\text{O} : \text{NH}_3 : \text{H}_2\text{CO}$ ices have also shown that two other organic compounds than POM are distinguished by infrared spectroscopy: methyleneglycol (HOCH_2OH) (Duvernay et al. 2014a, 2014b) and aminomethanol ($\text{NH}_2\text{CH}_2\text{OH}$) (Bossa et al. 2009b), which are the reaction products of H_2CO with H_2O or NH_3 , respectively (Fig. 11). The formation of such compounds in cometary environments is likely and therefore should be searched for by space missions dedicated to cometary analysis such as the *Rosetta* mission.

4.3.3 Formaldehyde Chemistry in Cometary Ices: HMT Formation

Formaldehyde is therefore a precursor for the formation of oxygen bearing compounds, but as we will discuss here, it is also a precursor for the formation of compounds bearing only nitrogen as a heteroatom. As previously mentioned, among the complex organic molecules present in the organic residues produced in the laboratory, hexamethylenetetramine (HMT, $\text{C}_6\text{H}_{12}\text{N}_4$) has been observed by numerous authors. It can reach up to 50 % of residue mass (Danger et al. 2013). HMT was initially proposed as a good tracer of photochemical processing in the pre-cometary phase (Bernstein et al. 1995) because it was supposed to be formed through the photolysis of the interstellar ice. However, HMT can be also formed either after proton irradiation of $\text{H}_2\text{O} : \text{CO} : \text{CH}_3\text{OH} : \text{NH}_3$ ices (Cottin et al. 2001) or by only heating at room temperature, without any energetic processing (photons or particles), of $\text{H}_2\text{CO} : \text{NH}_3 : \text{HCOOH}$ ices (Vinogradoff et al. 2011, 2012, 2013a, 2013b). Therefore, HMT cannot be considered anymore only as a tracer of photolysis. Furthermore, the thermal formation suggests that its formation cannot be explained only by UV photolysis processes. In fact, an association between UV and thermal processes should occur during the processing of a canonical $\text{H}_2\text{O} : \text{CO} : \text{CH}_3\text{OH} : \text{NH}_3$ ice mixture (Vinogradoff et al. 2013b). Indeed, this complex organic molecule has never been detected at low temperature after irradiation of interstellar/cometary ice analogues. It is only observed after the warming of a photolyzed-ice until 300 K. The mechanistic investigation of the HMT formation in such conditions allows elucidating the role played by irradiation and thermal processes. This mechanism is divided in two parts. The first part of this reaction occurs during the photolysis of the ice, where several photo-products are formed such as H_2CO and HCOOH . As described in Sect. 3.2.2, depending on the initial ice ratio, H_2CO can react with ammonia when the photolyzed ice is warmed, leading to the formation of $\text{NH}_2\text{CH}_2\text{OH}$. This molecule is then a bridge between POM-like structures $\text{H}_2\text{N}-(\text{CH}_2\text{O})_n-\text{H}$ and molecules bearing only nitrogen as an heteroatom. Since HCOOH is formed during the UV irradiation step, during the warming HCOOH catalyzes the $\text{H}_2\text{NCH}_2\text{OH}$ dehydration leading to the formation of methanimine CH_2NH . This imine formation opens a way through the formation of various linear or cyclic compounds bearing only C, H and N atoms. During this process, a specific cyclic intermediate can be formed, trimethylenetriamine (TMT), which is the last step for the HMT formation at around 300 K in laboratory conditions. The whole mechanism of HMT formation is displayed in Fig. 12.

Considering that the reaction has been performed in conditions that mimic those encountered in cometary environments, the HMT formation in such environments is likely, which thus justifies the fact that it will be searched for by the forthcoming *Rosetta* mission.

4.3.4 POM vs. HMT in Astrophysical Ices

POM and HMT are two very different complex molecules. POM is an oxygen-bearing polymer while HMT is nitrogen bearing cyclic molecule. However, as previously discussed,

Fig. 12 Formation mechanism of HMT in photolyzed cometary ices

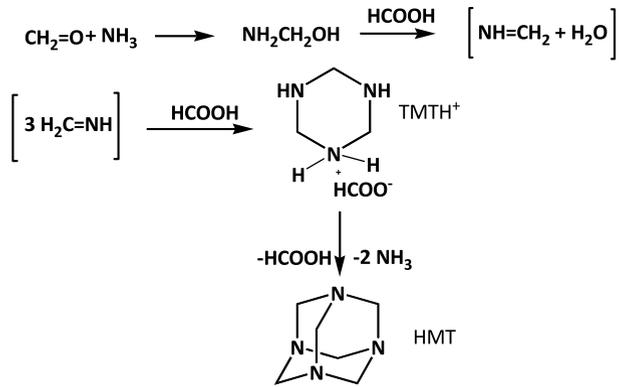
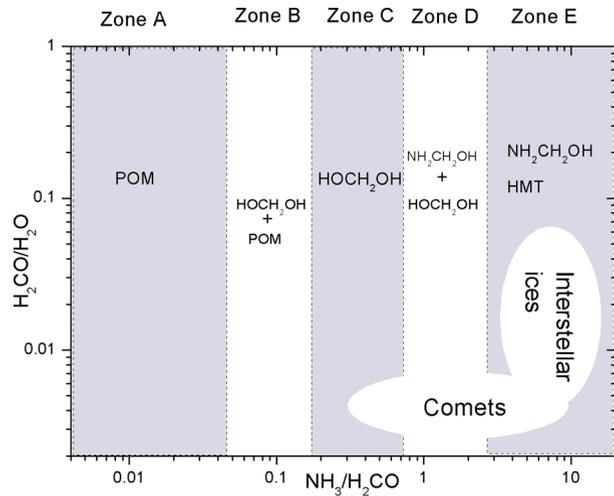


Fig. 13 The different major products formed from the warming of $\text{H}_2\text{O} : \text{NH}_3 : \text{H}_2\text{CO}$ ice mixtures as a function of the $\text{NH}_3 : \text{H}_2\text{CO}$ concentration and $\text{H}_2\text{CO}:\text{H}_2\text{O}$ concentration ratios. Horizontal and vertical ellipses represent the typical ice compositions detected in cometary environments and in star-forming regions. Reproduced from Duvernay et al. (2014a)



they both have the same precursor (Figs. 11 and 12): the formaldehyde H_2CO and their formation depends strongly on the initial ice composition and especially on the $\text{NH}_3/\text{H}_2\text{CO}$ ratio (see Fig. 13). The POM is only the major product when the $\text{NH}_3/\text{H}_2\text{CO}$ ratio is lower than 4×10^{-2} (zone A in Fig. 13), whereas the $\text{NH}_2\text{CH}_2\text{OH}$ (and thus the HMT since $\text{NH}_2\text{CH}_2\text{OH}$ is one of its precursors) will be the dominant product for an $\text{NH}_3/\text{H}_2\text{CO}$ ratio higher than 3 (zone E in Fig. 13). Therefore, the warming of interstellar/cometary ices may form $\text{NH}_2\text{CH}_2\text{OH}$ (and thus HMT if HCOOH is present) or POM, depending on the initial ice composition. An excess of ammonia in regard to formaldehyde would favor the $\text{NH}_2\text{CH}_2\text{OH}$ formation, while an excess of formaldehyde would favor POM formation. Shown in Fig. 13 (horizontal and vertical ellipses) are the $\text{NH}_3/\text{H}_2\text{CO}$ ratios and $\text{H}_2\text{CO}/\text{H}_2\text{O}$ ratios for several star-forming regions obtained from Spitzer data (Zasowski et al. 2009) (Öberg et al. 2011) as well as for cometary ices (Mumma and Charnley 2011). The typical ice composition of star-forming regions falls in the $\text{NH}_2\text{CH}_2\text{OH}$ domain (zone E in Fig. 13) while the typical cometary ice composition falls in both $\text{NH}_2\text{CH}_2\text{OH}$ and HOCH_2OH domains (zones C–E in Fig. 13). This means that cometary ices that are supposed to be formed from the accretion of primitive ices at the early stage of solar system formation may preferentially contain HOCH_2OH and $\text{NH}_2\text{CH}_2\text{OH}$ (and HMT). However, POM formation in

cometary ices cannot be definitively ruled out since the NH_3 column densities reported for star-forming regions in the literature are usually upper limits. Regions belonging to star-forming environments, where the NH_3 column density is low enough (compared to H_2CO) might exist and accordingly POM formation is plausible.

Thus the detection of both HMT and POM in cometary environments is not unlikely since cometary nuclei may have accreted matter coming from different disk regions with various ice compositions. In fact, the detection of POM and HMT (and its precursors) by the Rosetta mission will be another proof of the heterogeneity of the cometary nucleus composition. Since the ratio between these three products (POM, HOCH_2OH and $\text{NH}_2\text{CH}_2\text{OH}$) depends strongly on the initial ice composition (Fig. 13). Consequently, their detection could give information on the pre-cometary/interstellar ice composition.

5 Comet Outgassing

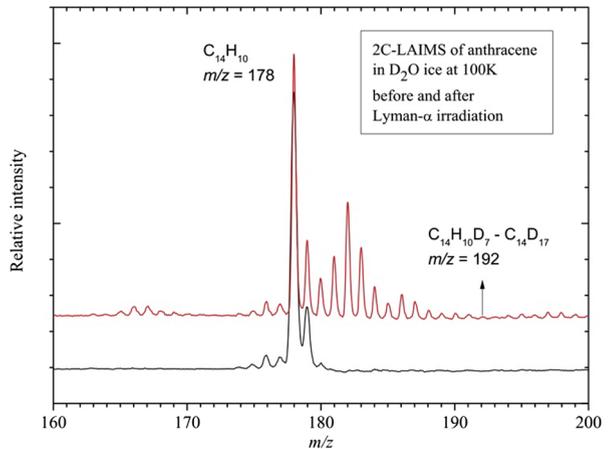
5.1 Isotopic Abundances and the Origins

It is customary to use isotopic abundances to date the materials (Aléon and Robert 2004; Alexander et al. 2010; Duprat et al. 2010; Lecluse et al. 1996; Tomescu et al. 2009) or to compare origins of different bodies such as planets, comets, asteroids, meteorites etc. (Feuchtgruber et al. 2013; Robert et al. 2000). Isotopes of trapped, unaltered materials that do not interact with their surrounding over astronomical time scales (Myrs to Gyrs) may carry information on their origin (Marty et al. 2008). However, when the material is continuously subjected to radiation and/or thermal processing (including sublimation) and exchange processes with its surroundings, the measured isotopic ratios may not be representative of the initial isotopic ratios of the materials. Then a detailed knowledge or estimation of the history of the body is necessary to extrapolate present day observed isotope ratios to early solar system conditions. Almost exclusively the D/H ratios observed for water have been made in the gas-phase ($\text{HDO}/\text{H}_2\text{O}$ line intensities), which may or may not represent the ice D/H ratios (vide infra).

Brown et al. (2012b) have shown from their laboratory work that when ice sublimation is much slower than molecular diffusion within the ice, enrichment of heavy isotope (D) occurs in the solid ice and lighter isotope (H) in the sublimed water—say in the case of a comet surface vs. coma/tail—hence the observations need to be carefully interpreted in the light of these laboratory data. In addition to thermally simulated altering the original isotope ratios, it is also possible to enrich or deplete heavier isotopes through radiation-induced processes. Photochemical enrichment of ^{13}C isotope in CO_2 solid films upon Lyman- α irradiation (10.2 eV) due to kinetic isotope effect has been reported by Yuan and Yates (2013).

Recently Yang and Gudipati investigated hydrogenated polycyclic aromatic hydrocarbons (PAHs) embedded in D_2O ice (Yang and Gudipati 2014). In the absence of any photons or electrons, no D/H exchange between the hydrogen of PAHs and Deuterium of the ice host could be observed (Fig. 14). As soon as UV or electrons were bombarded on the ice, an exchange between the H atoms of PAHs and D atoms of D_2O ice occurred, leading to almost complete deuteration of the PAH molecule. The same scenario can be reverted—when deuterium enriched organic molecule trapped in H_2O ice is subjected to radiation process, D of the organics will be exchanged with H of ice host, altering the D/H ratio of both the organics and the ice. Similar D/H exchange has been observed (Bernstein et al. 1999) when a room temperature residue was analyzed using laser ablation mass spectrometry of coronene ($\text{C}_{24}\text{H}_{12}$) trapped in D_2O ice, irradiated with UV and subsequently warmed

Fig. 14 Hydrogen enriched anthracene ($C_{14}H_{10}$) trapped in D_2O ice. No D/H exchange before UV irradiation (*black curve*). Upon Lyman- α irradiation both deuteration and D/H exchange occur resulting in a wide range of molecules with fractional deuteration and D/H exchange. Complete D/H exchange gives $C_{14}D_{10}$ ($m/z = 188$), complete deuteration + D/H exchange gives $C_{14}D_{20}$ ($m/z = 198$). Taken from Yang and Gudipati (2014)



up to room temperature—subliming the ice and leaving the non-volatile residue behind. Very recent modeling studies concluded negligible contribution from ionization-mediated chemistry towards deuterium enrichment in ices of a protostar (Cleeves et al. 2014).

Even in the absence of radiation or thermal processes exemplified above, under dark and cold environment, deuterium and hydrogen exchange can still occur through quantum chemical “tunneling” processes (Andersson et al. 2011; Hama and Watanabe 2013). Under these conditions reaction barrier for a D/H exchange through normal chemical potential is insurmountable, but because hydrogen atom acts as both a particle and a wave, there is a certain probability of hydrogen to move from one side of this energy barrier to the other side through the quantum chemical tunneling. Tunneling is temperature-independent. Hence tunneling could occur in the interstellar medium at 10 K or in KBOs or in comets, or in ices on Earth at 250 K with the same efficiency for a given system. Quantum chemical tunneling could thus lead to an exchange and mixing of D/H isotopes in the bulk ice even though it might have started with isotope enrichment at one location (such as in the case of a comet’s interior or on its surface). Based on the above recent experimental and theoretical data, it is necessary for the community to ensure that the observations made today can hold be compared to the times of their origin a few billion years ago.

5.1.1 D/H Ratios Measured on Comet Outgassing (Coma/Tail)

In spite of several observational data on the D/H ratios in interstellar and solar system water (mostly observed in the gas-phase), there is a critical need to get more observational data to improve the statistics and error bars, particularly for highly active solar system bodies such as comets. While the lower limit of deuterium abundance seems to be set by galactic and solar nebula D/H ratio of $\sim 2 \times 10^{-5}$, the upper limit observed so far in water seems to be $\sim 2 \times 10^{-2}$ in cold interstellar clouds. Water on Earth and comets (outgassing) fall in between at $\sim 1\text{--}3 \times 10^{-4}$. Recent Rosetta ROSINA data for the D/H ratio of water from the comet 67P/CG ($5.3 \pm 0.7 \times 10^{-4}$) puts the hypothesis—water on Earth could have come from comet impacts—to question. Data on the bulk ice D/H ratio in a comet’s nucleus is not available so far, as this can only be achieved through *in situ* sample analysis or cryogenic comet sample return. Once the planetesimals are formed there would be less direct radiation effect on the D/H ratios, but before their formation, in addition to the other processes mentioned above, radiation induced fractionation of D/H on a ice grain should also be taken into

account. The role of quantum chemical tunneling—that is temperature independent and can occur at the coldest, darkest parts of icy bodies with the same efficiency (Hama et al. 2014; Trixler 2013)—needs to be evaluated in the laboratory through experimental simulations.

5.2 Molecular Nitrogen in Comets

Contrary to CO, non-polar volatiles such as N₂ and O₂ have evaded direct observation through remote sensing due to their transparency in the infrared spectral region (Wyckoff et al. 1991). All these three molecules have similar volatility, suggesting N₂ and O₂ to be present in cometary nucleus, coma, and tail. Molecular oxygen is yet to be detected unambiguously, whereas Rosetta mission with its ROSINA instrument has successfully detected N₂ recently (Rubin et al. 2015), depleted by about a factor of 25 compared to protostellar N₂/CO ratio. A formation temperature of ~30 K is inferred from these observations, which could be explained by either amorphous ice with trapped N₂ and CO or crystalline ice with N₂ and CO clathrates. Though the observation of N₂ by Rosetta resolved the long-standing issue of “where is N₂”, the question of amorphous or crystalline interior is still open. Laboratory studies are necessary to address the question of D/H ratios as well as the N₂ vs. CO trapped in amorphous vs. crystalline ices.

5.3 Volatile Organic Compounds (VOCs) from Cometary Ice Analogs

5.3.1 Volatile Desorption from Water Matrix

The desorption of volatiles in comets is a complex phenomenon (Schaller and Brown 2007). Due to the size and mass of the comet, volatiles sublime and possibly form a vapor pressure controlled atmosphere, with a dynamical accretion-desorption phenomenon. Depending on the mass and temperature of the body, atmospheric escape can occur through a variety of processes, such as the Jean or the hydrodynamics escapes. On the microscopic scale, volatiles need to be accessible to the surface to desorb. They need to diffuse in the bulk of the cometary ice before reaching the surface. Their desorption processes are thus intimately linked to the water ice substrate (Jenniskens and Blake 1994). Amorphous water ice crystallization induces a fast release of the volatiles (Smith et al. 1997), the so-called molecular volcano process. Volatiles, which are not released through the diffusion-desorption process or the molecular volcano process are trapped in crystalline ice and will co-desorb along with the water ice mantle. The mechanisms for the entrapment of volatile gases trapped within amorphous solid water (ASW) have been studied by many authors (Notesco et al. 2003; Collings et al. 2003, 2004). This trapping of volatile gas in ice is of fundamental importance for chemical reactions and for the outgassing of interstellar ice in star forming regions and in comets (Marboeuf et al. 2012a, 2012b; Bar-Nun et al. 2013; Bar-Nun and Laufer 2013). The fraction of trapped volatiles within the ice and their release are depending on the thickness of the ice and on the heating rate (May et al. 2013a, 2013b). When extrapolating May et al.’s results (May et al. 2013b) to thick ice and to complex molecules, we can reasonably assume that co-desorption with the ice mantle dominates the volatile desorption. Another pathway to desorb volatiles from water ice is through photodissociation caused by vacuum ultraviolet (VUV) photons resulting in smaller atoms and molecules that escape the ice even at lower temperatures corresponding to larger heliocentric distances of a comet. For example VUV (63–310 nm) photochemistry of H₂O : CO₂ : NH₃ (1:1:1) ice produces H₂, NH₂, OH, O₂, and CO as volatiles exiting the ice (Chen et al. 2011).

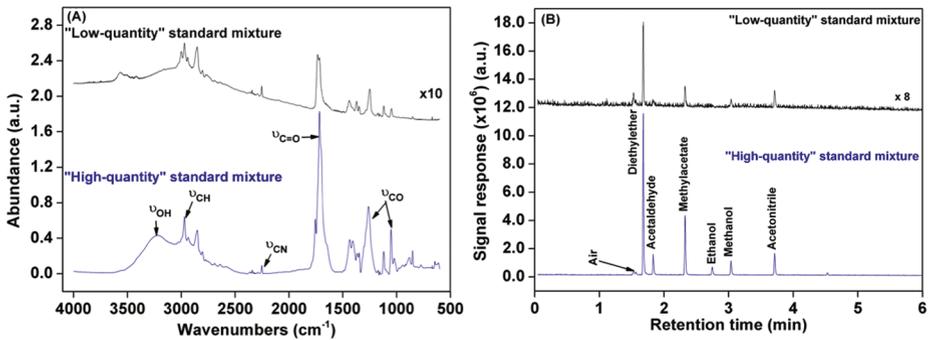


Fig. 15 Recovery of volatile organic compound (VOC) through the VAHIIA interface after their deposition on a cold finger (20 K) inside the vacuum chamber (10 mbar). Infrared spectra of ices (A) and GC-MS after the VOC recovery during the ice warming (B). Standard mixture used: diethylether, acetaldehyde, methanol, ethanol, methylacetate and acetonitrile. Reprinted with permission from Abou Mrad et al. (2014). Copyright 2014 American Chemical Society

5.3.2 Volatile Analyses from Ice Analogues

Some volatile compound analyses have been done on ice analogues, often on simple chemical systems, since their analyses with mass spectrometers (usually low mass resolution QMS) allow the confirmation of their identification previously obtained with infrared spectroscopy. As examples, it can be cited the glycine salt formation from a first thermal condensation of methylamine NH_2CH_3 and carbon dioxide CO_2 leading to the corresponding carbamate, followed by its UV irradiation forming this glycine salt (Bossa et al. 2009a); or the formation of aminoacetonitrile through UV irradiations of an acetonitrile and ammonia ice mixture (Danger et al. 2011b).

Volatile analyses have also been performed to understand products coming from thermal or photo-degradation of specific compounds such as polyoxymethylene (POM) or hexamethylenetetramine (HMT), that could explain the distribution of some species in comets such as formaldehyde or hydrogen cyanide (Cottin et al. 2000, 2002). These analyses were sometimes obtained by a direct mass spectrometer or by GC-MS after the condensation of volatile species on a cold finger and their subsequent warming (Cottin et al. 2000). Other authors used mass spectrometry for the study of gas trapping in water at low temperature (Notesco et al. 2003). However, no such studies were done for the characterization of volatile species coming from the heating of complex ice analogues, which are relevant to interstellar or cometary ices.

Recently, an analytical system devoted to the analysis of volatile organic compounds (VOC) has been developed (Abou Mrad et al. 2014). It consists in coupling a GC-MS system through a specific interface (the VAHIIA interface) to the vacuum chamber for obtaining an online analysis of these VOCs. The VAHIIA interface allows the recovery of VOC coming from the heating of cometary ice analogues and their subsequent transfer to the GC-MS for VOC separation and characterization. Using a standard mixture, this system was validated and has shown its ability to analyze and identify compounds deposited on the cold finger inside the vacuum chamber and subsequently warmed (Fig. 15). The forthcoming results will thus give important information on the reactivity that leads to residue formation. Furthermore, the GC-MS being a technique used and developed for space missions such as for the COSAC instrument on the Lander Philae of the *Rosetta* mission (Szopa et al. 1999,

2002a, 2002b, 2003), the VAHIA experiment should provide interesting information for the future data analyses coming from this mission.

6 Comet Coma and Tail

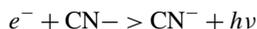
6.1 Negative Ions in Cometary Coma

An active positive-ion (cation) chemistry has long been known to occur in the collisional inner coma of comets (e.g. Rodgers et al. 2004). However, it is only recently that the possibility of an extensive negative-ion (anion) chemistry has been considered in theoretical models. Although several studies have been made, more experimental data on anionic processes involving cometary molecules are required. An important and unexpected discovery made by the RPA-1 electron analyzer on the *Giotto* spacecraft was the detection of negative ions (i.e., *anions*) in the inner coma of comet 1P/Halley: O^- , OH^- , C^- , CH^- and CN^- (Chaizy et al. 1991). Additional unidentified anions were also detected within the 22–65 and 85–110 amu (m/z) mass regions, leading Chaizy et al. to conclude that these were the negatively-charged versions of the complex ‘CHON’ organics detected in Halley’s coma (e.g., Altwegg et al. 1999). Prior to this, Wekhof (1981) had speculated on the possible presence of negative ions in cometary comae but, nevertheless, the Halley results came as a surprise. Subsequently, the presence of C_2^- has been claimed in optical spectra of comets Scorichenko-George (1990 VI) and C/2000 WM1 (LINEAR) (Churyumov et al. 1993, 2002).

Dalgarno and McCray (1973) and Herbst (1981) suggested that negative ions could be present in dense interstellar clouds and detailed predictions were made for specific species (e.g. Millar et al. 2000). These predictions were validated by the recent detection of anions in interstellar clouds and circumstellar outflows. The anions C_4H^- , C_6H^- , and C_8H^- have been detected in the envelope of the C-rich AGB star IRC+10216 (McCarthy et al. 2006; Cernicharo et al. 2007; Remijan et al. 2007); C_4H^- and C_6H^- are widespread in molecular clouds (Cordiner et al. 2013). Particularly relevant for comet chemistry is the fact that the emission line profiles in IRC+10216 indicate that the anions are forming in the region of the outflow where the interstellar UV radiation field is driving the chemistry. Bare carbon chains and various carbene (such as $H_2C = C = C:$) and cumulene (such as $H_2C = C = CH_2$) chains are detected directly in almost all comets (e.g., C_2 and C_3), are present as fragmentation products in the Halley data (e.g., C_4H), are suggested by the *Stardust* data, and are expected on the basis of interstellar chemistry (Mitchell et al. 1992; Altwegg et al. 1999; Geiss et al. 1999; Schleicher and Farnham 2004; Sandford et al. 2006). Thus, we should expect that a similar anionic photochemistry would also occur in cometary plasmas.

Amongst the various anion formation processes, three are most relevant for cometary comae:

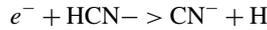
- (1) The elementary process of *radiative electron attachment*, REA,



is favored by a deep potential well for electron attachment (i.e., a large *electron affinity*, EA, of the neutral) and the presence of a large number of rotational and vibrational degrees of freedom for energy dispersal and IR photon emission. Competition with *electron autodetachment* from the intermediate activated complex leads to slow rates for radiative electron attachment to atoms and small molecules, $\sim 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. Organic radicals with significant EA values, and many internal degrees of freedom, can have

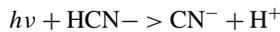
REA rates approaching the collisional rate of $\sim 10^{-7}$ – 10^{-8} $\text{cm}^3 \text{s}^{-1}$ (Herbst and Osamura 2008), making them prime candidates for anion formation by electron radiative attachment in dense, UV-irradiated astrophysical sources (Millar et al. 2007).

(2) *Dissociative electron attachment*, DEA



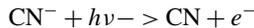
Experimental studies of DEA to acetylene and formamide have been performed (Szymanska and Mason 2011, Szymanska et al. 2014a, 2014b). In the former case product channels for both C_2^- and C_2H^- exist, suggesting that these anions may be present in cometary comae. Quantum-chemical calculations for rates of DEA and REA to long carbon-chain molecules that may be relevant to comets (polar and non-polar polyynes) have also been computed (Carelli et al. 2013a, 2013b).

(3) *Threshold ion-pair production* (TIPP; also called polar photodissociation),



should also be important in forming negative ions (Berkowitz et al. 1969; Massey 1976; Berkowitz 1979; Suits and Hepburn 2006; Hu et al. 2006). For example, Solar UV photons in the range ≈ 15.2 – 19 eV could produce CN^- from HCN .

The major loss route for cometary anions is *photodetachment*



The photodetachment cross-sections for small ions such as OH^- are large and yield rapid photodetachment rates in the unattenuated Solar UV field at 1 AU (Wekhof 1981). Complex molecules with higher EA values may have much lower cross-sections (e.g., Smith et al. 1978). The lifetimes of anions in the inner coma can be much longer than those calculated for the unattenuated Solar UV flux. Differential optical depth effects in the inner coma may tend to inhibit photodetachment, which destroys anions, but not substantially affect the TIPP processes forming them. Specifically, the high-energy photons, which drive TIPP, can penetrate deeper, producing anions in the dense, inner regions of the coma. The lower-energy photons, which cause photodetachment, however, will be absorbed in the outer coma.

These and other negative-ion processes were incorporated into the first model of cometary anion chemistry by Cordiner and Charnley (2014). Calculations showed that CN^- , C_4H^- , C_6H^- , and C_8H^- could all be expected to form in the coma and thus could provide candidate identifications for several of the peaks in the *Giotto* mass spectra at 1P/Halley. Anions may also be detected by the Rosetta mission to comet 67P/Churyumov-Gerasimenko. Part of the Rosetta Plasma Consortium, the ion and electron sensor (IES) contains two electrostatic plasma analyzers (one each for ions and electrons), operating over the energy/charge range 1 eV/e to 22 keV/e (Burch et al. 2007). Similar to the *Giotto* electron electrostatic analyser (EESA) that detected various negatively-charged molecules in the coma of comet Halley (Chaizy et al. 1991), the IES should have the capability of detecting negatively-charged particles in the coma of comet 67P, including molecular anions and negative nanograins (Goldstein et al. 2012). In contrast to *Giotto*, which traversed Halley's coma at about 68 km/s and was sensitive to negative ions with masses 1–830 amu, Rosetta's orbital speed with respect to the comet 67P/Churyumov-Gerasimenko will be small relative to the 1 km/s outflow velocity of the coma gases. It is therefore expected that the Rosetta IES will be sensitive to singly-charged negative ions in the coma with a higher mass range (190– 4.2×10^6 amu), covering large molecular anions and organic macromolecules with tens to hundreds of thousands of carbon atoms.

Thus, it is likely that any anionic molecular species detected by Rosetta would be derived from large organic compounds. Possible candidates are polycyclic aromatic hydrocarbons (PAHs), polymers of aliphatic and aromatic hydrocarbons, or polymers with highly polar/electronegative functional groups. PAHs are ubiquitous in many astrophysical environments and have previously been considered as components of cometary dust and ices (see review by Li 2009). Direct detection of PAHs in cometary comae is difficult and the tentative identifications of phenanthrene ($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$) in UV spectra of 1P/Halley, obtained by the Vega-2 spacecraft (Moreels et al. 1994; Clairemidi et al. 2004), remain inconclusive. Nevertheless, PAHs are clearly evident in the Stardust samples returned from comet 81P/Wild 2 (Sandford et al. 2006) and so they and their anions may indeed be found at 67P/Churyumov-Gerasimenko.

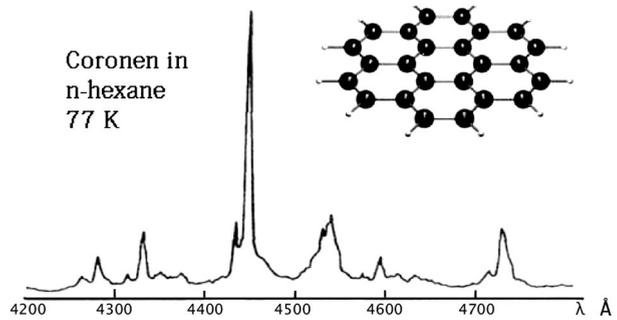
Development of coma chemistry models for PAH anion formation requires laboratory data and quantum-chemical calculations of the rates of anion processes. Some relevant work is the calculation of REA rates for phenanthrene, perylene ($C_{20}H_{12}$) and coronene ($C_{24}H_{12}$) by Carelli et al. (2013c). Experiments on DEA to PAHs have also been reported (Szymanska and Mason 2011). Future models of cometary anions will require more laboratory data and theoretical calculations on absolute cross sections and rates for anion chemistry involving abundant coma molecules. These will be particularly important if Rosetta detects anions in coma of comet 67P/Churyumov-Gerasimenko.

6.2 Fluorescence from Frozen Hydrocarbon Particles (FHPs) in the Coma and on the Surface

6.2.1 Emission Spectra of Active Comets

One of the most effective methods of cometary investigation is the spectroscopic observation of these bodies with subsequent analysis of the obtained data. Cometary spectra consists of two principal parts—emission lines and bands radiated by gaseous compounds of cometary comas, and faint solar continuum scattered by dusty and icy particles of the cometary halos. Gaseous comas are cool and rarefied shells around cometary nuclei and emit fluorescence on the specific wavelengths in UV, visible, and IR ranges of the electromagnetic spectrum. Daughter molecules as the result of photo degradation of parent species are main compounds of gaseous cometary comas. The following molecules and ions were already detected in comets: C_2 , C_3 , CH, CN, CO_2 , NH, NH_2 , OH, CH II, CO II (Arpigny 1995; Cochran et al. 2012). This list is incomplete, surely, being the subject of permanent growth. Parent molecule or their degradation products were detected as well in the cometary bodies, particularly, H_2O , HCN, C_2H_2 , CH_3OH , C_2H_6 , H_2CO and others (Mumma and Charnley 2011). The mineral and the icy halos of comets are clouds of fine dispersed grains responsible for the scattering of solar radiation. Gaseous comas and grains of halos form the cometary atmospheres as complex of gas and dust around icy nuclei. The cometary spectra are rich also with the series of narrow emission lines of unknown nature. These so-called unidentified emissions were registered in the spectra of many comets (Brown et al. 1996; Cochran and Cochran 2002; Cremonese et al. 2007; Kobayashi and Kawakita 2009; Dello Russo et al. 2013; A'Hearn et al. 2014). Many observers assigned these emissions to multiple ionized molecules (Wyckoff et al. 1999; Cochran and Cochran 2002; Kawakita and Watanabe 2002). New theory suggests luminescence nature of unidentified emissions in the form of photoluminescence by frozen hydrocarbon particles (FHPs) of cometary atmospheres (Simonia 2004, 2007, 2011a, 2011b, 2013). Approximately 10 % of the previously unidentified emissions were identified as photoluminescence of cometary

Fig. 16 Quasilinear photoluminescence spectrum of Coronene in n-hexane at 77 K (Shpol'skii 1960)



FHPs, though 90 % of the mentioned emissions remained in the status of unidentified and more laboratory work is needed to assign these emission bands. The peculiarities of cometary atmospheres provide the complicated character of cometary spectra in the form of various features superposition. The cometary nuclei are rich with complex organic substance (Ehrenfreund and Charnley 2000; Gudipati and Allamandola 2003; Clairemidi et al. 2004; Crovisier and Bockelée-Morvan 2007; Li 2009; Kobayashi and Kawakita 2009; Zellner et al. 2011).

6.2.2 Frozen Hydrocarbon Particles (FHP) in Cometary Coma

When the comets approach the Sun, processes of thermo destruction and sublimation of cometary ices are started. Micro fragments of nucleus ices form the spherical halo with various diameters. The sources of cometary hydrocarbons provide organic compounds for icy cometary halos as shells of frozen hydrocarbon particles (FHPs). Each FHP is characterized with inherent size, shape, and color. FHPs with substitutional solid solution structures have nano sizes, but molecularly dispersed FHPs micro sizes. Shapes of individual FHPs depend on structural peculiarities of icy particles. FHPs with substitutional structures may be flat, but molecular dispersed particles—bulky and elliptic.

The solar ultraviolet radiation excites FHPs, which produce photoluminescence cometary halos in range of 4000–8000 Å. Chemical compositions of cometary FHPs and physical peculiarities of Shpol'skii microcrystals have similar properties of their photoluminescence spectra including positions and profiles of emission lines. Photoluminescence spectra of the cometary FHPs at low temperature ($T < 80$ K) have the standard quasilinear forms—series of multiple narrow emission lines with average line width $\Delta\lambda \leq 1$ Å. Laboratory analogs of such spectra are called quasilinear photoluminescence spectra of Shpol'skii matrix (PAH in n-alkanes) (Fig. 16).

We also note that PAHs trapped and isolated in water-ice grains such as in ice particles in cometary tails also show strong photoluminescence properties, particularly their emission spectra very similar to gas-phase spectra but much broader due to inhomogeneous broadening (Allodi et al. 2013).

Photoluminescence spectra of the cometary frozen hydrocarbons could demonstrate also wide featureless bands (case of resonance dimmers). Such featureless bands may be observed as certain quasicontinuum. Similar phenomenon was reported by Churyumov and Kleshchenok (1999), Churyumov et al. (2013). On the other hand the width of emission lines and general character of photoluminescence spectra of Shpol'skii matrix depends also on temperature of polycrystalline substance. According to Shpol'skii (1959) acyclic matrix provides quasilinear character of frozen PAHs luminescence spectra. In case of glass-similar matrix the same PAHs demonstrates featureless photoluminescence emissions. For

the cometary case it means probably that quasi-continual luminescence emissions belong to amorphous mixtures of hydrocarbons. Narrow luminescence emissions indicate PAHs in n-alkanes matrix—crystalline FHPs. It might be the qualitative tool for remote determination of hydrocarbons state in the cometary matter.

Frozen hydrocarbon particles of the cometary halos interact also with gaseous compounds of comas. Physically such interactions are probably nonelastic in the form of absorption and adsorption of comas molecules by the solid substance of FHPs. Main result of the mentioned processes is enrichment and encapsulation of FHP substance with the neutral and ionic inorganic molecules of the cometary origin. Photoluminescence spectra of enriched organic probably differ from the original in positions and profiles of emission lines.

Solar UV and visible radiations probably excites also fluorescence of cometary solid organic in infrared range within 2–13 μm . FHPs of the cometary halos in this case as complex of fine dispersed icy grains are subject of the so-called infrared fluorescence phenomenon. Surfaces of cometary nuclei, including ice and mineral components are irradiated permanently by solar electromagnetic radiation and fluxes of the charged particles. Photo-processing and electrons bombardment of nuclei surfaces provides transformation of physical and chemical characteristics of surface substance. Within time scale of comets evolution the substance of nuclei surfaces is transformed completely due to external factors and forces. In other words, surface layers of the periodic comets nuclei contain new substance—the result of evolution. The substance of inner layers of the cometary nuclei including hydrocarbons, which have never been processed by the solar radiation, has primordial properties. Such a substance is called—the cometary relicts. The main properties of the cometary relicts are probably following: (a) extremely low temperature of the substance; (b) complex character of the substance with primordial structural peculiarities; (c) possible presence of prebiotic compounds.

6.2.3 *Frozen Hydrocarbon Particles in Cometary Jets and Flares*

In time of active cometary processes including flares and outbursts the certain fragments of relict substance (hydrocarbons mixtures) might be delivered in to the cometary comas. The solar radiation could excite photoluminescence and cathodoluminescence of newly delivered relicts. Depending on the chemical composition and the physical properties of the specific relicts such luminescence may be in the form of featureless emissions or highly structured quasilinear spectra. Duration of luminescence of the relicts may be rather short. The intense luminescence emissions of the relicts may be quenched by the solar infrared radiation. On the other hand, complex molecules of the same relict substance may be dissociated on daughter formations in the field of the solar hard ultraviolet radiation. Taking in to account high quantum yield of hydrocarbons luminescence we have proposed that ground based observations for registration of the relict substance luminescence must be made in time of outbursts or immediately after this phenomena. The cometary relicts in the form of clouds of icy micrograins will be processed by the solar radiation. Therefore, within 6–8 hours after outburst luminescence properties of relict substance will be lost or changed. The cometary outbursts or flashes spectra have character of featureless emissions in range 3900–5500 \AA (Cochran et al. 1980). Frozen organic mixtures, in certain cases, demonstrate photoluminescence spectra in the form of single bump in almost the same spectral range. Registration of photoluminescence of the cometary relicts including complex organic substance could become an effective tool for investigation of pristine matter of the Solar System including prebiotic compounds. This new conceptual hypothesis has been developed and presented by Simonia and Simonia (2013).

Table 1 Photoluminescence emissions in the spectra of Hyakutake comet

Cometary emissions (Å)	LabPhotolum lines (Å)	PAHs in n-alkanes	Reference
5102.235	5101.8	1-amino, 9, 10-anthraquinone + n-heptane	Nakhimovsky et al. (1989)
5110.064	5110	Naphtacene + n-nonane	Nakhimovsky et al. (1989)
5314.689	5315.4	9, 10-anthraquinone + n-heptane	Nakhimovsky et al. (1989)
5318.079	5318.1	2-methyl, 1, 4-naphtoquinone + n-hexane	Nakhimovsky et al. (1989)
5332.924	5332.5	1, 2-benzopyrene + tetrahydrofuran	Kirkbright and Lima (1974)
5909.68	5910	Tetraphene + n-hexane	Teplitskaiya et al. (1978)

6.2.4 Photoluminescence of Complex Organics of C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) Comets

The successful identification of previously unidentified cometary emissions is the important task for cometary organic investigations. Here two comets, namely C/1996 B2 Hyakutake and C/1995 O1 Hale-Bopp, are selected for identification of previously unidentified or unknown emissions. Morrison et al. (1997) observed Hyakutake comet with a Fiber-fed echelle spectrograph attached to the 1-m telescope of Ritter observatory at March 23 and 27, 1996; receiver—CCD; resolving power of spectrograph $R = 25800$; average signal-to-noise ratio was equal 200. Hyakutake comet was observed on the heliocentric distances $r = 1.08$; 1.00 AU. The mentioned authors found in the spectrum of Hyakutake comet the standard emissions of several molecules and ions. They revealed also 18 emission lines of unknown nature, which acquired the status of the unidentified emissions and used these lines for the comparative analysis.

Zhang et al. (2001) observed Hale-Bopp comet with a Cude Echelle spectrograph mounted on the 2.16 m telescope of Beijing astronomical observatory (Xinglong, China) at March 26, 28 and April 22, 1997; receiver—CCD; resolving power of spectrograph $R = 44000$; 37000 for the blue and red path; average signal-to-noise ratio was equal 180. Hale-Bopp comet was observed on the heliocentric distances $r = 0.920$; 0.918; 0.991 AU. The mentioned authors found in the spectra of Hale-Bopp comet the standard emissions of several molecules and ions. They revealed also 73 emission lines with unknown nature. For the comparative analysis works of Kirkbright and Lima (1974), Teplitskaiya et al. (1978), and Nakhimovsky et al. (1989) are referred to as the sources of laboratory data. These sources have been selected on the bases of supposition that substance of frozen hydrocarbon particles of the cometary atmospheres has the same structure as Shpolskii matrix—aromatic molecules trapped in n-alkane ices. The comparative analysis was made with the following strategy: (a) coincidence of the spectral positions of the observational and laboratory emission lines with accuracy of ± 1 Å; (b) profiles similarities of observational and laboratory emission lines.

All specific circumstances, including differences in wavelength scales, were taken in to consideration. The results of the comparative analysis for both comets are presented in Tables 1, 2.

In the spectrum of Hyakutake comet 18 emission lines were tabulated as unidentified (Morrison et al. 1997). We have identified 6 emissions as photoluminescence of PAHs fixed in n-alkanes. In other words 33.3 % of previously unidentified emissions represent photoluminescence of frozen hydrocarbon particles of icy halo of Hyakutake comet. In the spectrum of Hale-Bopp comet 73 emission lines were tabulated as unidentified (Zhang et al. 2001).

Table 2 Photoluminescence emissions in the spectrum of Hale-Bopp comet

Cometary emissions (Å)	LabPhotolum lines (Å)	PAHs in n-alkanes	Reference
4838.27	4838.2	Perylene + n-hexane	Nakhimovsky et al. (1989)
4850.66	4850	2-methylperylene + n-hexane	Nakhimovsky et al. (1989)
5318.19	5318.1	2-methyl, 1, 4-naphtoquinone	Nakhimovsky et al. (1989)
5333.01	5332.5	1, 2-benzopyrene + tetrahydrofuran	Kirkbright and Lima (1974)
5351.438	5352	Chrysene + n-hexane	Teplitskaiya et al. (1978)
5428.19	5427.5	1, 2-benzopyrene + tetrahydrofuran	Kirkbright and Lima (1974)
5909.64	5910	Tetraphene + n-hexane	Teplitskaiya et al. (1978)

We have identified 7 emissions as photoluminescence of PAHs in n-alkanes. 9.5 % of the total quantity of previously unidentified emission lines in the spectrum of Hale-Bopp comet represents photoluminescence of frozen hydrocarbon particles of icy halo of this comet (Table 2).

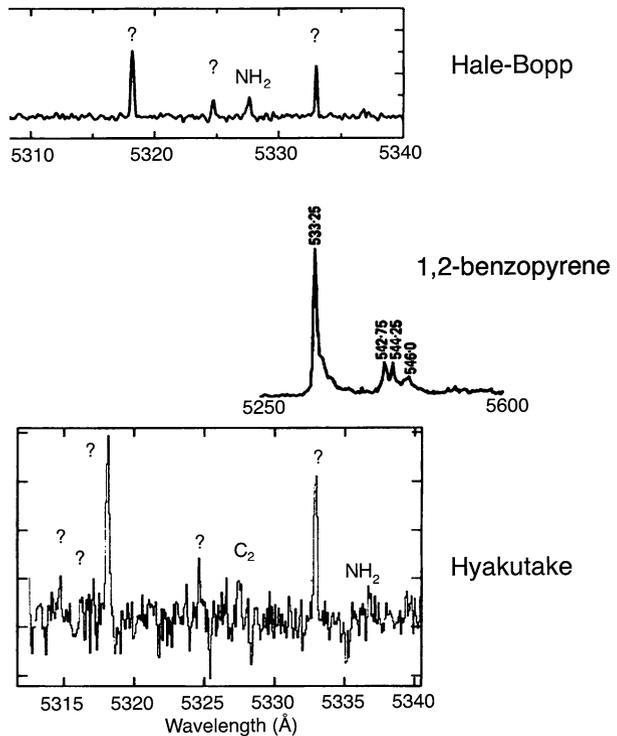
Figure 17 represents certain fragments of spectral profiles from Morrison et al. (1997), Kirkbright and Lima (1974), and Zhang et al. (2001), respectively. Photoluminescence emission line $\lambda = 5332.5$ Å of 1, 2-benzopyrene (Kirkbright and Lima 1974), coincides in spectral position and profile with previously unidentified emissions in the spectra of Hyakutake and Hale-Bopp comets. Other emission lines of these comets spectra also coincides in spectral positions and profiles with laboratory photoluminescence emission lines of PAHs in n-alkanes. In fact the substance of Hyakutake and Hale-Bopp comets is rich in complex organic in the form of frozen mixtures of aromatic and acyclic hydrocarbons. The inner layers of Hyakutake and Hale-Bopp comets nuclei contain the bulk organic zones—sources of hydrocarbons. Organic relicts are delivered from cometary nuclei in to atmosphere on the short heliocentric distances as the natural markers of the Solar System past.

In other words, Schpol'skii matrix in the form of frozen polycrystalline mixture (prebiotics in n-alkanes) luminesces as series of very narrow emission lines. In this case luminescence of such mixtures is excited by ultraviolet radiation. It means that series of very narrow emission lines of the cometary spectra (early unidentified emissions) might belong to luminescence of FHPs with prebiotic compounds. Results of the comparative analysis and this hypothesis has been obtained, developed, and presented by Simonia and Simonia (2013, 2014).

6.2.5 Implications to Detection of Aromatic Molecules on Comets

The frozen hydrocarbons are components of cometary ice. The cometary substance is probably rich in the complex aromatics and acyclics. These hydrocarbons are comprised unified structures including solid solutions, polycrystalline mixtures, and substitutional matrices. The potential cometary prebiotics or biotics are related with the complex organic. Therefore the significance of remote revealing of complex organic of comets is high. The intense solar ultraviolet radiation, the fluxes of charged particles, and the structure of cometary organic substance provide bright luminescence phenomena of cometary organic ice with possibilities of its detection. We have suggested that Shpol'skii matrix in the form of polycrystalline mixtures (PAHs in n-alkanes) might be the main unit of cometary complex organic substance.

Fig. 17 Unidentified emissions in spectra of Hale-Bopp (5333.01 Å) and Hyakutake (5332.92 Å) comets; Luminescence of 1, 2-benzopyrene (5332.5 Å)



Frozen hydrocarbon particulate (FHP) matter of the cometary nuclei will be the main source of fine dispersed organic icy particles of the cometary halos. In time of the cometary outbursts or flares the certain portions of cometary relict matter penetrates in to cometary comas with subsequent photo-excitation of this matter. The de-excitation of previously excited molecules (relict molecules) will be accompanied by bright luminescence emission. Optical spectra of the cometary bursts could be rich in unknown emission lines or featureless bands especially in the blue range. Photoluminescence spectra of polycyclic aromatic hydrocarbons at temperatures $T > 100$ K has featureless character in the form of extended blue emission (4000–4900 Å). In our opinion for the first time this extended blue emission of the cometary spectra was registered by Bobrovnikoff (1927a, 1927b). In terminology of Bobrovnikoff “violet type spectra” were registered for the several comets. Archived spectroscopic data of the cometary outbursts or flares must be reanalyzed in light of this problem.

We have also described the cometary FHPs with molecularly dispersed structure and substitutional solid solution structure. Both molecular systems have binary nature. The first class of the icy particles consists of aromatic molecules (guest) fixed in whole acyclic matrix (host). The second class of the icy particles consists of aromatics (or carbon rings) substituted in acyclic chains. Such solids belong to the so-called Shpol'skii matrix, which is the source of bright luminescence in the field of UV radiation. We have studied the spectra of Hyakutake and Hale-Bopp comets in search of FHPs photoluminescence emissions. The comparative analysis of the optical spectra of the mentioned comets with photoluminescence spectra of FHPs laboratory analogs was performed. For Hyakutake comet 6 previously unidentified lines were identified as cometary FHPs photoluminescence. For Hale-Bopp comet—7 emissions were assigned to photoluminescence of frozen hydrocarbon particles of icy halo.

The main properties of analogs of frozen hydrocarbon matter of comets discussed here show the possibilities of revealing of prebiotics as pristine matter of the Solar System. Several unidentified emission bands from comets could be associated with laboratory spectra of PAHs trapped in Shpol'skii organic matrix, and new suppositions were presented. Photoluminescence has been shown to be an important molecular property to investigate and identify cometary organic matter. At the same time we are rather far from the complete understanding of cometary organics' nature and its interactions with external forces. More laboratory photoluminescence data is needed on realistic analogs of cometary ices interacting with organics, minerals, and radiation and UV wavelengths that simulate solar spectrum also into the vacuum ultraviolet region ($\sim 100\text{--}300\text{ nm}$).

7 Conclusions

In this review we have shown that though our understanding of comets has tremendously improved in the past decades, several key questions remain unanswered, for which serious answers can only be obtained with cryogenic comet subsurface sample return (CCSSR) missions. Until then the composition and geology of a comet nucleus remains a puzzle, including whether water-ice exists in amorphous or crystalline phase, whether clathrates can exist or even dominate the nucleus, etc. Crystalline ice alone does not trap large quantities of impurities (volatiles) within the lattice, resulting in the volatiles to be expelled into ice grain boundaries. How such a scenario would fit into observation of outgassing of short period comets needs to be explored both in the laboratory and through modeling studies. Water and volatiles condensed at very low temperatures forming high-volatile-content amorphous ice grains (similar to interstellar ice grains) explains readily many observed phenomena of comets. Crystalline water-ice can not be ruled out, but to explain large quantities of trapped volatiles it is necessary to invoke clathrates that are formed at higher temperature and pressure or condensation of volatiles along with crystalline ice grains at very low temperatures ($\sim 30\text{ K}$). Laboratory measurements on the thermal properties of realistic cometary analogs have begun and need to be intensified in order to constrain the same on comets. Thanks to extensive efforts made in the laboratory, we have now a better understanding of the breadth of volatile and non-volatile organics that can be formed on the surface and near surface. While PAHs may be potential candidates to be looked at for both their emission as FHP or as negatively charged ions in cometary coma, cometary surface and crust could host a suite of organic matter from abiotic to prebiotic to biogenic. Many of these molecules have been detected and analyzed in the laboratory on cometary ice analogs. A few observations on isotope enrichment (D/H ratio) from comets seem to fall in a range (within a factor of 2–5) of terrestrial D/H ratio. While the observations are robust, how to interpret them in connection with the origin of our solar system seems to be heavily debated. More laboratory work is warranted in this connection, especially taking into account potential channels of equilibration, exchange, and defractionation.

Since the beginning of 2015 science results from the Rosetta mission are becoming public. In addition to being the first ever landing on a comet surface (unlike impacting a comet during the Deep Impact mission), Philae revealed unexpected hardness of comet 67P/CG shell, which could be understood as being due to hard crystalline ice beneath the expelled organics during warm-up of its surface as the comet's surface gets warmer. Long-standing hypothesis that comet's dark low-albedo surface is organic-rich, is proven by Rosetta's VIR-TIS observations. However, it still remains unresolved what is the molecular composition of these organics, for which more observations and perhaps future comet surface sample return

(touch-and-go) could help. Laboratory studies are also critical to evaluate a wide range of conditions and compositions possible to interpret the observed spectra. For a better understanding of the interior, we still need to wait for final results from the CONSERT results to be published. Microwave sounder instrument (MIRO) on Rosetta measured low thermal inertia of 67P/CG, in accordance with the expected low-thermal conductivity and high porosity of cometary surface dust. Most surprising results also came from the ROSINA mass spectrometer—that water from 67P/CG is highly enriched with heavier isotope D, putting these observations to the highest deuterium enrichment observed so far indicating extremely cold interior preserving high-deuterium content from interstellar ices. This observation is in line with the detection of N₂ and the evaluation of N₂/CO ratio leading to ~30 K as the temperature of cometary core during its formation. Each of these observations raise more questions, for which we also future comet missions, particularly that perform in-situ analysis of subsurface composition of a comet at least a meter or two deep and bring back these cryogenic comet samples at ~30 K leading us in to the next-generation comet science.

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