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Physics and chemistry of icy particles in the universe: answers from microgravity

P. Ehrenfreund^{a,*}, H.J. Fraser^b, J. Blum^c, J.H.E. Cartwright^d, J.M. García-Ruiz^d, E. Hadamcik^e,
A.C. Levasseur-Regourd^{e,f}, S. Price^g, F. Prodi^h, A. Sarkissian^e

^a*Leiden Observatory, P.O. Box 9513, NL-2300 RA Leiden, The Netherlands*

^b*Raymond & Beverly Sackler Laboratory for Astrophysics, Leiden Observatory, P.O. Box 9513, NL-2300 RA Leiden, The Netherlands*

^c*Astrophysikalisches Institut und Universitäts-Sternwarte, Schillergaessen 2, D-07745 Jena, Germany*

^d*Instituto Andaluz de Ciencias de la Tierra, Laboratorio de Estudios Cristalográficos, Facultad de Ciencias, Av. Fuentenueva s/n,
E-18002 Granada, Spain*

^e*Service d'Aéronomie/CNRS, Route de Gatines, BP 3, F-91371 Verrières le Buisson, France*

^f*Université P. et M. Curie, Paris VI, 4 Place Jussieu, F-75005 Paris, France*

^g*Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

^h*Institute of Atmospheric and Ocean Sciences, Via P. Gobetti, 101, C.A.P. I-40129 Bologna, Italy*

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Abstract

During the last century, the presence of icy particles throughout the universe has been confirmed by numerous ground and space based observations. Ultrathin icy layers are known to cover dust particles within the cold regions of the interstellar medium, and drive a rich chemistry in energetic star-forming regions. The polar caps of terrestrial planets, as well as most of the outer-solar-system satellites, are covered with an icy surface. Smaller solar system bodies, such as comets and Kuiper Belt Objects (KBOs), contain a significant fraction of icy materials. Icy particles are also present in planetary atmospheres and play an important role in determining the climate and the environmental conditions on our host planet, Earth. Water ice seems universal in space and is by far the most abundant condensed-phase species in our universe. Many research groups have focused their efforts on understanding the physical and chemical nature of water ice. However, open questions remain as to whether ices produced in Earth's laboratories are indeed good analogs for ices observed in space environments. Although temperature and pressure conditions can be very well controlled in the laboratory, it is very difficult to simulate the time-scales and gravity conditions of space environments. The bulk structure of ice, and the catalytic properties of the surface, could be rather different when formed in zero gravity in space.

The author list comprises the members of the ESA Topical Team: Physico-chemistry of ices in space. In this paper we present recent results including ground-based experiments on ice and dust, models as well as related space experiments performed under microgravity conditions. We also investigate the possibilities of designing a new infrastructure, and/or making improvements to the existing hardware in order to study ices on the International Space Station (ISS). The type of multidisciplinary facility that we describe will support research in crystal growth of ices and other solid refractory materials, aerosol microphysics, light scattering properties of solid particles, the physics of icy particle aggregates, and radiation processing of molecular ices. Studying ices in microgravity conditions will provide us with fundamental data on the nature of extraterrestrial ices and allow us to enhance our knowledge on the physical and chemical processes prevailing in different space environments.

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* Corresponding author.

E-mail address: pascalle@strw.leidenuniv.nl (P. Ehrenfreund).

1. Introduction

1.1. Ices throughout the universe

Ices are observed throughout the universe: on planetary bodies, comets, in the interstellar medium (ISM) and in protoplanetary disks. In cold, dense regions of the ISM ($T = 10$ K, $\rho = 10^6$ H atoms cm^{-3}) ices are formed by efficient accretion of atoms and molecules from the interstellar gas onto carbonaceous or silicate dust particles. Once adsorbed on the surface of such interstellar grains, small molecules and atoms diffuse across the surface layer and form more complex molecules via catalytic reaction pathways (Ehrenfreund and Charnley, 2000). Regulatory mechanisms such as selective thermal desorption, sublimation, bulk diffusion, and grain explosions return molecules back to the gas phase. The evolution of interstellar icy grain mantles is determined by the local environment, which can be quiescent or dominated by shocks (including high temperatures) and UV (ultraviolet) irradiation. Dense interstellar clouds are themselves the birthplace of stars. These clouds collapse under their own gravity, to form new stars (protostars) surrounded by a protostellar disk, from which stars, planets and small bodies form, within an evolutionary period of $\sim 10^{6-8}$ years. Infalling interstellar dust and gas are processed according to the local physical and chemical conditions, which are in turn dependent upon the distance from the forming star. It is assumed that in the local vicinity of the protostar (within 5 AU, Astronomical Units) thermal desorption dominates the chemistry and all ices are evaporated (e.g. Markwick et al., 2002). Further out in the protostellar disk, where temperatures are low enough, volatile species may recondense, forming a ‘new generation’ of icy grains beyond the snowline. Turbulent mixing of materials from the inner solar system region with the outer has been postulated as a reasonable explanation for the presence of crystalline silicates in comets (Bockelee-Morvan et al., 2002).

Molecular ices are also widespread in the solar system. They cover the poles of terrestrial planets (e.g. Earth, Mars). Mars has permanent ice caps at both poles, composed mostly of solid carbon dioxide. Recent data from the high-energy neutron detector (NASA Mars Odyssey mission) show substantial amounts of hydrogen extending 60 degrees from the poles (Feldman et al., 2002). Hydrogen-rich regions have also been identified near the poles with the γ -ray spectrometer, indicating the presence of subsurface ice (probably in the form of water). Most of the outer solar system bodies are covered with ices, predominantly water-ice, although more volatile species can be trapped on (and in) solar system bodies such as Triton and Pluto under very low temperature conditions (i.e. < 60 K) (Schmitt et al., 1998; Roush, 2001; Ehrenfreund and Fraser, 2003). A number of the Galilean satellites of Jupiter have been visited by several spacecraft. In particular, Europa’s icy surface has been studied

in detail to establish whether it is possible for a subsurface ocean to be present (Greely et al., 1998). A large number of small bodies formed in the outer solar system, e.g. comets and Kuiper Belt Objects (KBOs), are composed predominantly of icy material (Schmitt et al., 1998). The ring system of Saturn is very bright (albedo 0.2–0.6) and contains a mixture of innumerable rocky and icy particles. For a discussion of planetary ices we refer the reader to recent review articles in Schmitt et al. (1998). In this paper we focus on the influence of low-gravity environments and therefore on icy particles in the ISM, ices covering regolith on small solar system bodies and icy particles that agglomerate to make cometary nuclei. We also discuss icy particles that exist in planetary atmospheres, including our own. They are vital to the Earth’s climate because of their radiative properties and play a significant role in atmospheric chemistry because of heterogeneous reactions that can take place on their surfaces.

A number of molecular ices are present in space environments on particles in the ISM, our solar system and in the Earth’s atmosphere, e.g. CO_2 , H_2O , CH_3OH , NH_3 , and CH_4 . Astronomers use the term ‘ice’ to refer to any of these condensed solids, frozen out from their volatile gas counterparts. Each of these solids can exist in a number of crystalline or amorphous solid phases, and the links between these solid, gas and liquid phases are typically represented on a pressure–temperature phase diagram. Amorphous ices resemble liquids, in that they exhibit no long-range molecular order. Provided that the temperature is low enough to prevent molecular rearrangement from occurring, the amorphous ices are metastable with respect to the crystalline forms. The presence of crystalline ices infers that the pressure and temperature conditions under which the ices formed were somewhat higher than the prevailing conditions during amorphous ice formation. It can also be an indicator of pressure, stress or elevated temperature on the ice itself, driving the phase change from amorphous to a crystalline form.

Fig. 1 summarizes the distribution and physical properties of icy particles in our own galaxy and solar system. In low-temperature astronomical environments, water ice is present in its amorphous form, (see Fig. 1(a) and (b)). The solid ice phases form from vapour deposition of gas-phase H_2O molecules onto cold substrates or by reactions on the grain surface. Crystalline phases of water ice have also been observed in several space environments (including circumstellar shells, moons, Saturn’s rings and comets) indicating that these environments are, or have been (at some time), under higher temperature and/or pressure conditions (see Fig. 1(a–c)). In planetary atmospheres the icy particles can be crystalline or amorphous: a third generation of supercooled particles may also be present, formed by rapid cooling from the liquid phase (see Fig. 1(d)).

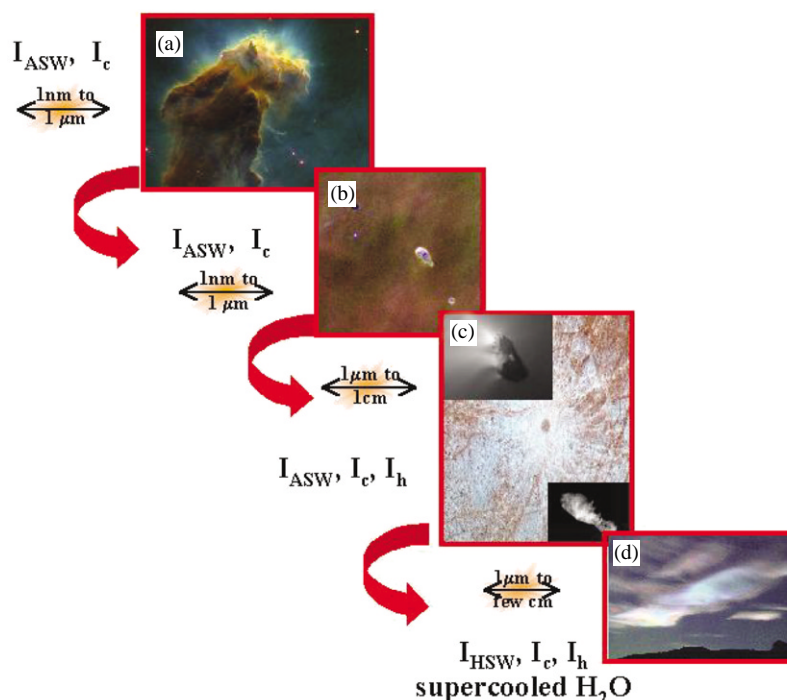


Fig. 1. The evolution of icy particles from the interstellar medium to planetary atmospheres, showing the key water ice phases and grain sizes at each stage. I_h = hexagonal ice, I_c = cubic crystalline ice, I_{ASW} = amorphous ice (deposited from vapour phase), I_{HSW} = amorphous ice (formed by hypercooling liquid phase) (see text for details). (a) Icy mantles form on dust particles in interstellar clouds, through condensation from the gas phase, or by reactions on the grain surfaces. (b) As dense cores within interstellar clouds collapse, icy grains are incorporated in the coldest regions of the disk. Closer to the protostar, icy mantles are evaporated and reform as the disk cools. (c) Over a few million years, the dust aggregates, form small planetesimals, and subsequently planets. The remaining planetesimals form the population of comets and asteroids, the surfaces of which may be covered with regolith and ices. (d) Many planets and moons within our own solar system are known to have ices on their surfaces and in their atmospheres. On Earth, icy particles are known to form in various clouds from water vapour and supercooled liquid water. These icy grains are a key constituent of Polar Stratospheric Clouds (PSCs), that themselves play a major role in the chemistry of our upper atmosphere. Credits: (a) Jeff Hester and Paul Scowen (Arizona State University), NASA; (b) D. Johnstone (CITA), J. Bally (U. Colorado) et al., WFPC2, HST, NASA; (c) PIRL, Galileo Project, NASA, Halley Multicolor Camera Team, Giotto Project, ESA, Deep Space 1 Team, JPL; (d) P. Newman and R. Kawa.

1.2. The phase diagram of water

Throughout the universe, H_2O is by far the most common ice, and also the most widely studied. H_2O has a complex phase diagram, due to hydrogen bonding and proton disorder effects (see Fig. 2). It exhibits an extensive range of crystalline solid phases, most of which form under high pressure. The physical properties of the water ice, such as density, conductivity, vapour–pressure and sublimation rate, are dictated by its crystalline structure. The phases can be distinguished from each other by the arrangement of H_2O molecules in the solid lattice, and the degree of proton disorder within the lattice. In all crystalline H_2O ices, the H_2O molecules have 4-fold coordination, donating two hydrogen bonds, and accepting two others, even if the bonds are distorted. The phases themselves are numbered in the order they were discovered, and therefore no link can be made between the name, and structure or behaviour of an ice phase. Most phases are thermodynamically stable under a limited range of pressure–temperature conditions, with some phases also exhibiting metastable phases, and a few having no regions of absolute stability at all. The prevailing temperature and

pressure conditions in our galaxy under which icy particles form, result in the formation of hexagonal, I_h , cubic crystalline, I_c , or amorphous phases of H_2O –ice. Fig. 2 summarizes in a ‘flow chart’ rather than a traditional phase diagram the phases of water–ice that are relevant in the remainder of this paper, as well as the prevailing formation conditions.

In the laboratory, at temperatures below 70–80 K and low pressures, vapour deposition of water onto a cold substrate results in the formation of a highly microporous amorphous ice, called amorphous solid water (I_{ASW}). The structure can essentially be thought of as fractal (like an ‘icy foam’), with a huge specific surface area (typically $4000 \text{ m}^2 \text{ g}^{-1} \text{ cm}^{-2}$) and the ability to adsorb and trap gaseous species. This ice closely resembles high-density amorphous ice I_{hda} (density 1.1 g cm^{-3} ; which is formed from I_h under very high pressures) but there is some doubt as to whether it is identical! At around 77 K (and atmospheric pressure), I_{hda} transforms, irreversibly, to its analogous low density form, I_{lda} (density 0.94 g cm^{-3}). Similarly, I_{ASW} undergoes a gradual, but irreversible, collapse of its micropore structure between 35 and 65 K under low pressure conditions, also converting to a lower density form (Jenniskens et al., 1995). Again

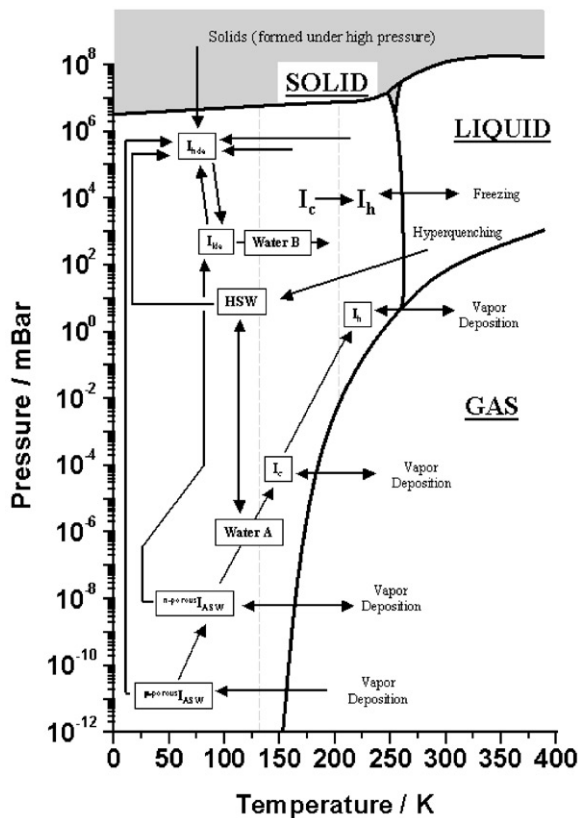


Fig. 2. A figurative phase diagram of water at low temperatures highlighting the amorphous phases. The figure refers to phases of thin films under laboratory conditions on Earth: supercooled liquid phases also exist when I_h particles are cooled. Note that the phase transitions represented are illustrative, and not necessarily indicative of the specific pressure and temperature conditions where a phase transition occurs. Single headed arrows represent irreversible phase changes, double headed arrows reversible processes, (see text for further details).

this nanoporous I_{ASW} resembles, but is almost certainly not the same as, I_{lda} . The restructuring of water ice has significant relevance for the trapping and release of volatiles within the matrix (Collings et al., 2003). Much confusion exists in the literature between the definitions associated with the various forms of amorphous water ice: generally the terms are applied quite liberally and interchangeably. In fact, ices formed by low-temperature and low-pressure vapour deposition should always be referred to as I_{ASW} , whereas other amorphous phases of H_2O ice that are produced by compressing (at high pressure and low temperature) stable crystalline phases such as I_h , should be referred to as high-density amorphous ice, I_{hda} , and low-density amorphous ice, I_{lda} . These distinctions are outlined clearly on the phase diagram in Fig. 2, and the nomenclature described above will be used throughout the remainder of this article.

In the laboratory, under low pressure conditions, amorphous ices transform directly into cubic crystalline ice, I_c (Smith et al., 1997) between 120 and 140 K. Before crystallization occurs, the ice goes through the glass transition where it forms a viscous liquid (Smith and Kay, 1999). However, most laboratory researchers heat the ice so rapidly

that this glass transition can therefore not be observed, and the amorphous ice appears to transform directly to the cubic crystalline form. Ices produced in the cubic phase always transform irreversibly to hexagonal ice, I_h , at 200 K. If this ice I_h were then cooled below 72 K, it could form the proton ordered form of I_h , ice XI, but, in a pure ice the molecular relaxation rate is too slow for this process ever to take place. It can however be mediated by doping the ice with OH^- ions, which are relatively mobile in the ice, even at 72 K.

The hexagonal form of water ice, I_h , is thermodynamically the most stable form of ice and predominant in the terrestrial environment. To summarize, when H_2O ices are formed by vapour deposition at low pressure in the laboratory, amorphous ice is formed below 130 K, I_c is formed between 130 and 160 K and I_h is formed above 160 K. These temperature values can vary slightly with pressure, but form a suitable guide. Some of the recovered high density phases, frozen in liquid N_2 and then gently warmed, also form this metastable cubic phase.

The formation of icy particles from existing solid or liquid phases is as complex as condensation from the gas phase. Bulk water ice can never be cooled into a glassy solid state or an amorphous ice, as crystallization always occurs first. Supercooled liquid droplets, however, can also form amorphous solid particles when cooled rapidly in a cold air or cryogenic liquid flow: this phase is generally referred to as hypercooled solid water I_{HSW} (Petrenko and Whitworth, 1999). This resembles a route by which supercooled ice particles might form in the Earth's upper atmosphere. At room temperature, high pressure conditions can be used to convert bulk samples of I_h into ice II, III or IX, but it has been shown that if icy particles of I_h are compressed, a supercooled liquid is formed, which when cooled below 150 K can then form I_c or I_{hda} . The latter can also be formed directly by compressing particles of I_h which have first been cooled to below 150 K.

Although I_{HSW} and I_{ASW} represent distinct phases of water ice, it is however likely that many similarities will exist between the amorphous solid phases observed in extraterrestrial ice particles and icy particles in planetary atmospheres (such as our own). Our current understanding of extraterrestrial ices relies entirely on data compiled from laboratory-based studies (Earth, therefore at 1 g). Open questions remain as to whether ices produced in Earth laboratories are also good analogs for ices produced in space environments. Experiments that evaluate the physical and chemical properties of the ice surface or bulk are generally performed with thin film ice layers, supported by a chemically inert substrate, rather than isolated particles. Such experiments do indicate that the diversity of amorphous water ice in our universe is far greater than most astronomers or atmospheric scientists currently contemplate, and, given the range of extreme conditions under which ices are forming, it is quite possible that amorphous ice structures exist, where the ices have been under conditions quite difficult to recreate on Earth. Experiments on aggregation processes,

or light scattering properties require small particles or levitating clouds of particles (Levasseur-Regourd et al., 1998).

Ice studies under microgravity conditions therefore offer significant advantages:

(i) In microgravity and reduced gravity environments, no weight-induced compaction occurs in low-density ice aggregates or ice-aggregate layers. This ‘lack’ of compaction has been demonstrated in previous studies of the formation of highly porous dust aggregates, which are compacted when gravity overcomes the inter-particle rolling-friction forces (Blum and Wurm, 2000). On the other hand, on the molecular scale, better layer organization and a reduction in defect sites can also result in crystalline ices forming structures that more closely resemble theoretical models. Such materials can display different optical properties, different physical properties, and larger void volumes than those grown on Earth (Ahari et al., 1997, see also Section 6). These differences, resulting entirely from the strength of the gravitational field, are attributable to the different transport regimes that dominate solid formation in the presence and absence of gravity. In particular, the suppression of convection and dominance of surface tension effects are particularly important in substances whose crystal structure is determined by weak inter-layer or inter-molecular interactions. Since this is the case for ices, one would expect ices formed in microgravity or reduced gravity also to possess structures with different physical properties from those grown on Earth.

(ii) Under long-duration microgravity conditions icy particles are isolated and free-floating for a sufficient time that their spectroscopic and optical properties can be measured (Levasseur-Regourd et al., 1998, 2001). Microgravity conditions actually allow light scattering measurements to be performed on low-concentration particle cloud, without any multiple scattering induced by sedimentation. During aggregation, size-discrimination effects between particles, and convective heat-transfer processes, are suppressed. In microgravity surface-tension effects are particularly prevalent during melting, and may also play a role in determining the reactivity and ionization potential of the surfaces of icy particles.

(iii) Compared to terrestrial levitation experiments with, e.g., aerodynamic or electrostatic levitation techniques, under reduced gravity conditions, no separation between different ice particle sizes or shapes occurs (e.g., due to variations in surface-to-mass or charge-to-mass ratio) in ice-cloud aggregation experiments.

(iv) No particle alignment (for non-spherical ice particles) will occur in ice cloud experiments under microgravity conditions for uncharged ice grains as opposed to experiments in the lab, in which the ice particles will be aligned due to their sedimentation velocity and the interaction with ambient gas (Wurm and Blum, 2000).

By studying the surface and bulk morphology of molecular ices in microgravity over a range of pressure and temperature conditions, we will be able to emulate amorphous ice morphologies in other regions of our universe. This includes the characterization of icy aerosol particles, which

play an important role in Earth’s climate system and in atmospheric chemistry. This research offers us a novel insight into the formation, existence and destruction of molecular ices in exceptional environments. In this paper we discuss recent laboratory experiments investigating the structure and surface chemistry of interstellar ice analogs with particular emphasis on H_2 formation (Section 2), laboratory simulations on the formation of planetesimals (Section 3) and light scattering experiments on cometary analogs (Section 4). Section 5 discusses experiments and related models in atmospheric chemistry. An overview of recent experiments performed under microgravity conditions is given in Section 6. We conclude with future perspectives on microgravity research in Section 7.

2. Interstellar ice chemistry in the laboratory

The interstellar medium takes up a few percent of the mass of a galaxy and is composed of gas and dust. The majority of the gas consists of H ($\sim 75\%$) and He atoms ($\sim 25\%$), followed by small amounts of O , C and N . The most abundant molecule is H_2 (discussed in Section 2.1) followed by CO , which is around 10,000 times less abundant. About 1% by mass of the interstellar material is micron-sized dust particles, (silicates or carbon-based), which are interspersed in the far more abundant interstellar gas. Whereas the large voids of interstellar space are too hot to allow molecular condensation and ice formation, the dense interstellar medium represents an environment where ices are stable and efficiently formed. Almost all atoms and molecules freeze out onto dust particles in such environments, where the temperatures can be as low as 3–10 K (Ehrenfreund and Schutte, 2000; Ehrenfreund and Charnley, 2000). The freeze-out of these species depends on the sticking probability, i.e. the likelihood that when an atom, molecule or radical collides with the bare grain, or ice surface, it remains “frozen out” on the surface. It is usually assumed that under interstellar conditions this probability is 1, i.e. everything that collides with the grain sticks. However, there must be cases where the sticking probability is less than 1.

At relatively low temperatures (10–30 K) atoms such as H , D , C , O and N have sufficient energy to diffuse and react on the surface of grains. Many molecular species are likely to be formed in catalytic gas-surface reactions on dust grains in the interstellar medium. This heterogeneous chemistry occurs in two ways:

- (i) direct (Eley–Rideal) mechanisms, where collisions between gas-phase radicals, atoms or ions and the grain (ice) generate new molecular species, or
- (ii) indirect (Langmuir–Hinshelwood) mechanisms, mediated by photon, phonon, electron, or thermally induced processes, where one or both reagents diffuse across the grain surface until they encounter each other, react and generate new molecules.

In this way simple molecular species such as H_2O , NH_3 , or CH_4 can be formed by exothermic hydrogenation reactions. The composition of the ice layers is strongly dependent on their local environment and they may contain predominantly hydrogen rich (H_2O -dominated with traces of CO , CO_2 , CH_4 , NH_3 , CH_3OH , HCOOH and H_2CO) or CO -dominated (with certain amounts of N_2) ices. Successive ice layers of different composition build up as the grains travel through star-forming regions, which are characterized by different temperatures and density conditions. The Infrared Space Observatory (ISO) has been used to measure the environment of dense clouds and has contributed greatly to our current understanding of interstellar ice chemistry (Ehrenfreund and Schutte, 2000; Gibb et al., 2000).

The precise factors initiating and limiting the ice mantle growth are not yet understood. What is clear is that icy grain mantles play a key role in the chemical evolution of dense interstellar regions. We lack knowledge on both the kinetics and thermodynamics that describe how these chemical reactions would proceed under the harsh interstellar and star-formation conditions. This is made even more complex given a lack of information on the physical attributes of such ice particles and thin films. The ice morphologies in these environments depend on the prevailing pressure, temperature, and gravitational conditions. In turn, many of the ice's physical properties are directly dependent on this morphology, e.g. density, porosity, vapour pressure, conductivity, sublimation rates and stability. All of these behavioural properties can directly affect the chemistry, which means that we also have to understand the underlying physical behaviour of the systems we are looking at.

In order to identify species, to measure their column densities in space and to define the physical and chemical properties of interstellar ices, laboratory experiments that simulate space conditions are essential (Ehrenfreund and Fraser, 2003). Low-temperature infrared spectroscopy is an effective technique that has been used to study the spectroscopy of ice analogues typical of the interstellar medium as well as solar system objects. Pseudo interstellar conditions are recreated at temperatures of 10 K and pressures of $< 10^{-6}$ Pa (10^{-8} mbar). However, the time scales of reactions in space environments can only be poorly reproduced by simulations in terrestrial laboratories. For example, the accretion time in dark clouds is statistically one atom per day and the lifetime of a cloud is $\sim 10^7$ years.

A number of laboratory studies have been undertaken to study the surface chemistry occurring on interstellar ice analogues. Hiraoka et al. (1994) demonstrated that hydrogenation of CO to CH_3OH via H_2CO can occur at 10 K. Although they derived a low total yield for methanol production, this may be related to the difference between laboratory and interstellar timescales discussed above, since in the laboratory most accreting H atoms will react with another H atom to form H_2 before they have a chance to react with CO or H_2CO . Further experiments by the same group have shown that hydrogenation of O, N, and C atoms occurs

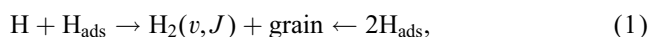
efficiently, and that C_2H_2 can be reduced to C_2H_6 (Hiraoka et al., 1995, 2000).

The chemistry of icy grains is strongly influenced by the environmental conditions. Thermal processing close to the star leads to molecular diffusion and structural changes within the ice matrix. Ice segregation, and possibly even clathrate formation has been observed in dense clouds (Ehrenfreund et al., 1998). In the laboratory, thermal processing of ice mixtures containing H_2CO and NH_3 has been found to result in polymerization of the formaldehyde into polyoxymethylene (POM; $(-\text{CH}_2-\text{O}-)_n$; (Schutte et al., 1993). Energetic processing of ices may have only limited influence on the ice chemistry due to the strongly attenuated UV irradiation in dense clouds, but cosmic rays can penetrate through clouds and ice surfaces and certainly modify structure and composition of icy particles, including sputtering of the particle surfaces. In the laboratory it would only be possible to study pseudo interstellar icy particles if they were isolated in magnetic or ion traps (therefore requiring the grain to carry charge). Given the technological and experimental complexities of trying to work with such systems no data yet exist from experiments of this kind, although Gerlich and coworkers at the University of Chemnitz have embarked on an ambitious programme of this nature. Consequently, we have little knowledge on the microscopic ice structure of icy interstellar particles, the effect of particle size can have on chemical rates, nor on the effects of thermal or energetic processing when the energy is dissipated in a small isolated grain, rather than a substrate supported thin film. Work in microgravity or reduced gravity, where such icy particles could be suspended indefinitely without the aid of a trap, would allow us to reveal the physical properties and structure of such icy particles, and should be one of the future goals of microgravity research.

2.1. The formation of H_2 on interstellar dust

Molecular hydrogen is by far the most abundant molecule found in interstellar space and has been observed in gas clouds in the interstellar medium (ISM) through rocket borne spectroscopy (Carruthers, 1970), satellite spectroscopy (Hurwitz, 1998) and Earth based observations (Gautier III et al., 1976). Due to its high abundance molecular hydrogen is a crucial participant in all of the chemistry in the ISM and the molecules generated by this chemistry provide a crucial cooling mechanism during the gravitational collapse of molecular clouds to form stars (Williams and Hartquist, 1999). However, the problem of how to form molecular hydrogen with a high enough efficiency to account successfully for its abundance in the ISM is a major problem in modern astrochemistry (Williams and Hartquist, 1999) as the relevant gas phase reactions are inefficient under the conditions prevailing in the ISM. The widely accepted mechanism for the formation of H_2 in the ISM is that it forms through a catalytic reaction between H atoms

(H_{ads}) on the surface of cosmic dust grains *via* reaction



where the grains are thought to be either carbonaceous or silicate in nature and may have icy mantles. Note that the H₂ product may be formed in a variety of ro-vibrational states which are classified by their vibrational quantum number v and their rotational quantum number J .

Many of the facts required to fully understand the formation of H₂ on dust grains are yet to be determined. How efficient is the reaction? What happens to the 4.5 eV binding energy released upon formation of the H₂ molecule; does it go into heating the grain or does it provide internal excitation of the newly formed H₂ molecule? What is the effect of the nature of the dust surface on the energy balance of the formation reaction and the efficiency of H₂ formation? These questions are vitally important for understanding the observations of H₂ and for modelling chemical processes in the ISM.

To date, some progress has been made in understanding H₂ formation on cosmic dust in the ISM both theoretically and experimentally. Theoretically, both classical (Rutigliano et al., 2001; Takahashi et al., 1999a, 1999b) and quantum mechanical models (Farebrother et al., 2000; Jeloica and Sidis, 1999; Meijer et al., 2001; Sha and Jackson, 2002) predict significant excitation of the product molecules. Experimentally, other groups have studied the formation of H₂ and HD under interstellar conditions on olivine (Biham et al., 1998; Pirronello et al., 1997a,b), amorphous carbon (Gough et al., 1996; Katz et al., 1999; Pirronello et al., 1999), and typical icy mantle surfaces (Manico et al., 2001), but no determination of the ro-vibrational distribution of the product molecules has yet been carried out.

The experimental apparatus (Perry et al., 2002) consists of three parts: a “source” chamber containing an atomic hydrogen source, the output of which is piped, using a polytetrafluoroethene (PTFE) tube (hydrogen atom recombination on clean PTFE is very inefficient), to an aluminium tube attached to a liquid helium cold head. The aluminium tube is used to cool the H atom beam without causing significant recombination. The hydrogen atom beam then passes, via a skimmer, to the “chopping” chamber containing a series of turning fork choppers, which can be inserted into the hydrogen atom beam generated from the source chamber. Following the chopping chamber the beam reaches the “reaction” chamber containing a time-of-flight mass spectrometer (TOMS) and a target mount attached to a second, helium cooled (10 K), cold head. In the experiments described in this paper, the hydrogen atom beam is piped from the downstream side of the skimmer up to the target using a PTFE tube. The cosmic dust targets are mounted on the end of the cold head. With the sublimation pump running, the reaction chamber achieves a base pressure of around 10^{-8} Pa (10^{-10} mbar). Rigorous testing shows that this experimental arrangement does not produce any vibrationally excited H₂ in the incident H-atom beam and hence any vi-

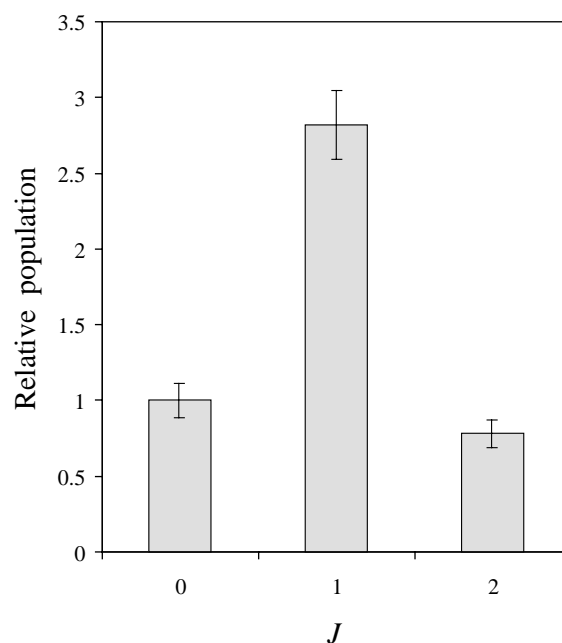


Fig. 3. Measured relative rotational populations, J , for H₂ ($v=1$) formed by the reaction of room temperature H atoms on an highly orientated polycrystalline graphite (HOPG) surface at 40 K.

brationally excited H₂ we observe must come from recombination on the target.

In the reaction chamber we probe the ro-vibrational distribution of the H₂ formed in excited vibrational states using resonance enhanced multi-photon ionization (REMPI). In this spectroscopic technique H₂ is state-selectively ionized using a pulsed laser and the resulting ions detected using a time-of-flight mass spectrometer (TOFMS). Molecular hydrogen formed in $v=0$ cannot be probed due to the significant signals from the background gas in the chamber which is also in $v=0$.

Current experiments have concentrated on the formation of H₂ on graphite (HOPG—Highly Orientated Polycrystalline Graphite) and Fig. 3 presents the ro-vibrational distribution we observe in $v=1$ following recombination of a room temperature H atom beam on HOPG at approximately 40 K. Clearly, vibrationally excited H₂ is being formed. Considering the energy balance in this formation process, the shapes of the H₂⁺ signals in the TOFMS clearly indicate that the H₂ ($v=1$) is not formed with a large translational energy, certainly less than 0.9 eV. Hence, it is apparent that much of the available energy (> 50%) from the formation of the H–H bond is going into the surface.

The above result, which indicates significant energy flow into the surface, is in good agreement with the conclusions of mass spectrometric temperature programmed desorption (MS-TPD) experiments which indicated that a significant percentage of the H₂ formed on amorphous carbon under pseudo-astrophysical conditions remained on the surface and was not immediately desorbed (Katz et al., 1999). Such a significant residence time clearly indicates some accommo-

dation of the 4.5 eV of internal energy from the nascent H₂ molecule into the surface.

2.2. Open questions and future work

Clearly, the temperature of the surface (40 K) is rather high in comparison with the interstellar dust we are attempting to simulate. In this temperature regime theoretical studies indicate that H atoms do not possess enough energy to chemisorb (Jeloaica and Sidis, 1999; Sha and Jackson, 2002). In addition, if the physisorption well is as shallow as experiment and theory indicate, the H atom coverage may well be low (Ghio et al., 1980; Jeloaica and Sidis, 1999; Katz et al., 1999; Sha and Jackson, 2002). Indeed, the modelling of the H₂ formation process using the kinetic parameters extracted from the MS-TPD experiments indicated that H₂ formation should be very inefficient at 40 K (Katz et al., 1999). Hence, we may see a significant increase in the signal strength when we move to lower temperatures. However, it is hard to reconcile the significant energy transfer to the surface that we observe, which implies strong H₂-surface coupling, with a situation where the reactant H atoms are only held in a physisorbed well. Perhaps, at the low H-atom coverages and “elevated” temperatures the reactivity is dominated by processes at defects where there is a smaller barrier to initial H-atom chemisorption.

The experiments are in their early stages and a great deal of further work is required. The effect of surface temperature on the H₂ ro-vibrational distribution needs to be probed and a new target mount has just been installed which should reach 10 K. In addition, the effect of the nature of the surface on the H₂ ro-vibrational distribution needs to be investigated. It is certain that interstellar grains are coated with water (and other) ices in many environments and, hence, the nature of these surfaces may well affect the energy budget in the H₂ formation process. Obviously, experimental evidence concerning the nature of the ice surfaces which form on interstellar grains under microgravity is important in guiding laboratory experiments, such as ours, to study the internal energy distribution of H₂ formed on interstellar grains.

3. Formation of planetesimals and cometesimals

Star formation occurs through the gravitational collapse of a rotating individual galactic molecular cloud core. This occurs when the cloud core is no longer supported against gravity by gas pressure, turbulent motions or magnetic fields. The region collapses from the inside out and, due to the conservation of angular momentum, the accretion onto the protostar is flattened. In this early stage, the so-called protostellar phase, the forming star is therefore surrounded by an accretion disk of infalling gas and dust. It has been one of the most important observational discoveries of the last decade that most pre-main-sequence objects show a disk (Dutrey, 1999). Planets form in such circumstellar gas-dust disks around young stars. In a first stage, the initially

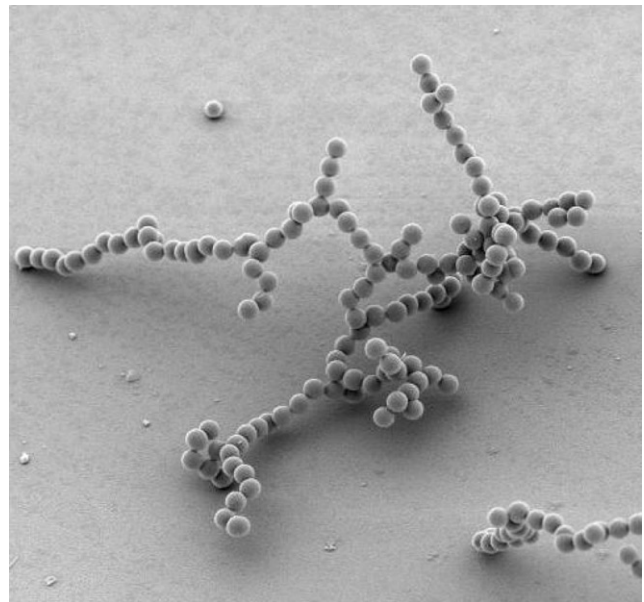


Fig. 4. SEM picture of a fractal dust agglomerate consisting of monodisperse, spherical SiO₂ particles of 0.95 μm radius. This dust agglomerate formed due to differential sedimentation in a laboratory experiment.

microscopically small dust grains (typical size 1 μm) collide gently due to Brownian motion, differential drift motions and gas turbulence (Weidenschilling and Cuzzi, 1993), and agglomerate due to adhesive surface forces (like, e.g., van der Waals force and hydrogen bonding). When the so-called planetesimals, kilometre-sized planetary precursors, have formed, mutual gravitational interaction leads to a rapid further growth to planetary sizes (Wetherill and Stewart, 1993). While the physics of the latter stage is rather well understood, the theory of the formation of planetesimals still bears major uncertainties.

In the past years, considerable progress in understanding the formation of decimetre-sized dust agglomerates in the young solar system has been made, basically due to extensive laboratory work (see Blum, 2000). It is now clear that micrometre-sized silicate particles adhere to one another due to van der Waals force (Heim et al., 1999) and that the velocity threshold for sticking is typically a few m s^{-1} (Poppe et al., 2000). Dust-cloud experiments have shown that low-velocity collisions in ensembles of particles lead to a rapid growth of fractal dust agglomerates (see Fig. 4). The fractal dimension D_f —the exponent in the power-law relation between agglomerate mass m and agglomerate size s , $m \propto s^{D_f}$ —depends on the velocity field between the agglomerates in the dust clouds. For Brownian-motion-driven agglomeration at the earliest stage of planetesimal formation, $D_f \approx 1.3$ (Blum et al., 2000), whereas for slightly larger aggregates differential sedimentation and gas turbulence lead to somewhat higher fractal dimensions of $D_f \approx 1.8$ (Blum et al., 1998) and $D_f \approx 1.9$ (Wurm and Blum, 1998), respectively.

The predicted collision velocities in the solar nebula exceed the limit for impact restructuring, when the fractal

agglomerates reach centimetre size (Blum and Wurm, 2000). As a consequence, the fractal dimension gradually increases to $D_f = 3$, for which the dust agglomerates are no longer fractal but are roundish bodies with a constant (and possibly high, 85%) porosity. Due to the decrease in surface-to-mass ratio, the decimetre-sized dust balls drift considerably faster than their fractal counterparts. Thus, the collision velocities exceed the fragmentation limit (Blum and Wurm, 2000) without considerable increase in size, resulting in the generation of impact debris and thus in a widening of the size spectrum.

The further growth of dust agglomerates between 0.1 and 1000 m is unclear, because the average collision velocity is higher than the velocity threshold for sticking. However, experiments suggest that the interaction with the ambient gas could lead to a trapping of fragments from high-speed collisions (Wurm et al., 2001a, b). A detailed modelling of this growth stage is still lacking.

3.1. Open questions

It should be noted that the entire experimental work is based upon the agglomeration of *refractory* dust particles. The mutual interactions between micrometer-sized *icy* particles and agglomerates thereof have not yet been investigated under the conditions of the outer solar nebula. Adhesive forces and sticking thresholds for icy grains, their agglomeration behaviour at various velocities, restructuring and fragmentation thresholds for icy agglomerates, and the importance of sintering for the outcome of collisions are the primary open questions that should be addressed in the near future. These questions are not solely of academic nature but are of the utmost importance for the formation of comets and the origin of comets, KBOs, the icy moons of the outer solar system, and possibly even for the cores of the giant planets.

4. Comets and asteroids

Cometary nuclei are minor solar system bodies, composed of ices (mostly H_2O) and organic-silicate dust particles, which aggregated at the epoch of pre-planetary formation. Some minor bodies which orbit far away from the Sun (e.g. Kuiper Belt Objects) are likely to be also icy bodies, even if they do not exhibit any cometary activity and may be called asteroids. Cometary ices are predominantly water ice; but by now more than 25 other small molecules have been identified (Crovisier and Bockelee-Morvan, 1999). It is not known whether pristine cometary ices are crystalline or amorphous. Lellouch et al. (1998) observed crystalline water ice emission from small grains in the coma of Hale-Bopp. However, they inferred temperatures of ~ 150 K for these grains, which would mean that the crystallization could have occurred very recently.

The D/H ratio in water (of about 3.1×10^{-4} , as measured for comets Halley, Hyakutake and Hale-Bopp) is consistent

with a formation of cometary water ice in a cold interstellar cloud (Meier and Owen, 1999). Glassy silicate grains (so-called GEMS for glass with embedded metal and sulphides) found in some interplanetary dust particles collected in the Earth environment are likely to be of interstellar origin (Bradley, 1995). These observations (see e.g. Altwegg et al., 1999) agree with the scenario of refractory grains produced in stellar envelopes being nuclei for the condensation of molecules, with the resulting particles later processed by cosmic radiation and finally agglomerated to form cometary dust particles.

We have very little knowledge on the composition and properties of cometary nuclei and lack in particular information on how the large amount of icy material is mixed with the more refractory material. Moreover, cometary nuclei, which may be built up of smaller cometsimals, seem to be stratified in density, porosity and temperature (Klinger et al., 1996, Prialnik and Podolak, 1999). Currently, the molecular inventory of cometary ices is inferred from observations of the coma, which allow us to establish a general inventory of the nuclear ice composition. However, laboratory studies have shown that surface layers of comets become relatively rapidly depleted in ices and the outgassing is subsequently controlled by the sublimation of volatiles from subsurface layers. The rate at which volatiles are released depends on the enthalpy of sublimation, which in turn is dependent on the microscopic structure of the ice. Therefore it is crucial to obtain a better understanding of the ice morphology in comets. Several important results have been obtained, during the last year, in cometary sciences, especially through the inter-comparison of the numerous observations of Comet C/1995 O1 Hale-Bopp. The frequent occurrence of fragmentation events, corresponding to the release by cometary nuclei of icy fragments with sizes in the 100–5 m range, or even below, (Desvoivres et al., 2000) emphasizes the importance of estimating the fragmentation threshold for icy agglomerates. The discovery of regolith on a small near Earth asteroid (433 Eros), with dust concentrated in craters by electrostatic charging, suggests the existence of icy regoliths on remote asteroids (e.g. Centaurs, KBOs), whose surface properties need to be assessed.

4.1. Polarization measurements

The refractory component of comets, i.e. cometary dust, is only known from the particles ejected in the coma when the comet approaches the Sun. These solid particles are observed by different methods, providing ideas on their possible physical properties. It has been observed that the particles are not the same in different regions of the coma (Levasseur-Regourd et al., 1999). Polarimetric maps of the light scattered by dust are appreciable diagnostics of these differences (Renard et al., 1992; Hadamcik et al., 1997).

Numerous observations of the degree of linear polarization of solar light, scattered by dust, in cometary comae (hereafter called polarization) have been performed by

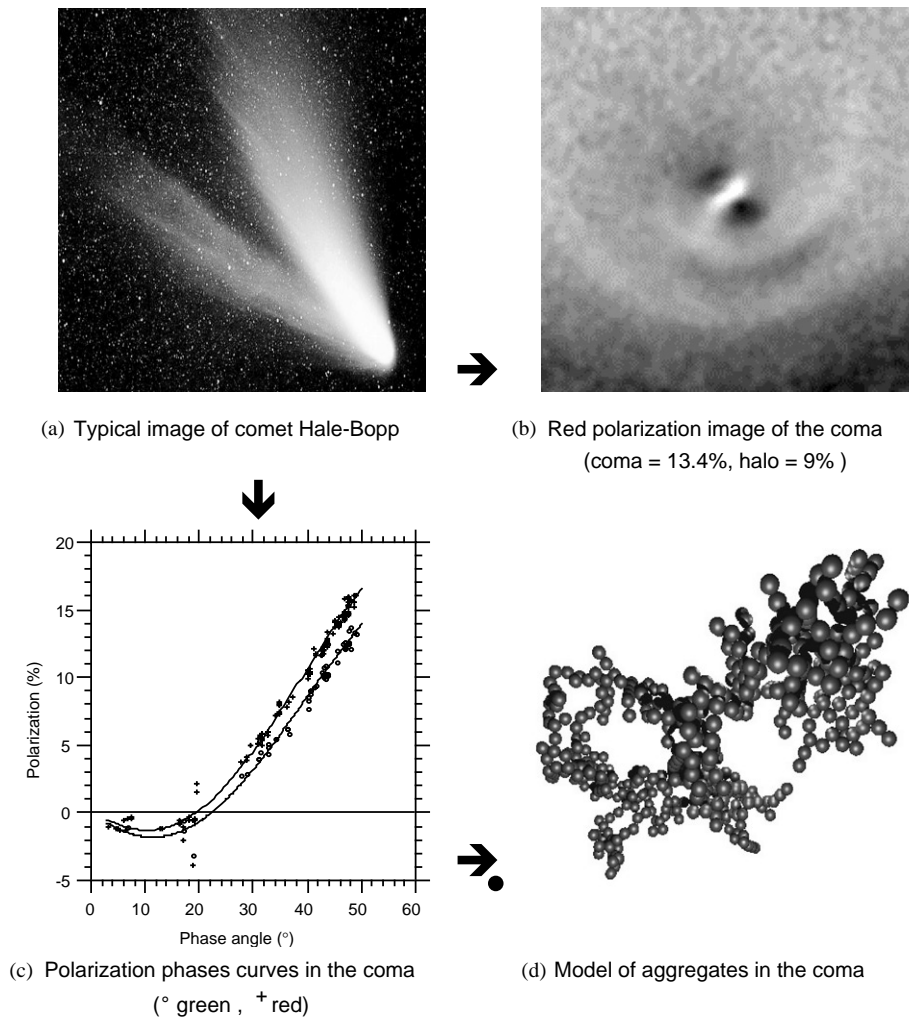


Fig. 5. (a) Comet nuclei, built up of ices and dust, partially evaporate near their perihelion and give rise to comae and tails of gas, ions and dust particles (credit: A. Dimai, Col. Druscic Obs.). (b) Polarization images of the coma (here Hale-Bopp at 43° phase angle) reveal differences in the physical properties of the dust, with a lower polarization in the inner coma that (together with a change in the polarization colour) suggest the presence of icy particles. (c and d) The colour of the polarization phase curves retrieved mostly in the outer coma is typical of very fluffy (possibly fractal) dust aggregates of submicron-sized grains that could be remnants of more compact particles after sublimation of their ices.

different teams. Polarization data, which mainly depend upon the phase angle and the wavelength, allow us to point out at least three classes of comets: (i) comets with a low maximum, (ii) comets with a higher maximum and (iii) comet C/1995 O1 Hale-Bopp, the polarization of which is always the highest in the positive branch (Levasseur-Regourd, 1999).

Cometary polarization usually increases with the wavelength. Comet Hale-Bopp observations (Hadamcik and Levasseur-Regourd 2003) may be used to derive accurate fits in different wavelength ranges. The corresponding phase curves are similar. In the visible domain, the (linear) increase in polarization corresponds to a slope of about 14% per micron for Hale-Bopp for a phase angle equal to 50° . However, the wavelength dependence of the polarization could follow an opposite trend in the vicinity of the nucleus (Jockers et al., 1997), in agreement with what was revealed

by Giotto in-situ observations of 1P/Halley (Hadamcik, 1999). The presence of freshly ejected ices (Renard et al., 1996) could actually induce such an effect. Fig. 5 presents the different cometary regions and the results of polarimetric observations.

Laboratory measurements performed for two wavelengths on clouds of levitating particles with the PROGRA² experiment (Worms et al., 2000) show that compact dust particles induce a blue polarization colour while mixtures of fluffy aggregates of sub-micron sized grains of silica and of carbon, which agglomerate in highly porous structures, induce a red polarization colour (Levasseur-Regourd and Hadamcik, 2001; Hadamcik et al., 2002a). The blue polarization colour suspected in the vicinity of cometary nuclei could be a clue to the presence of large compact particles hovering above the nucleus, or of freshly ejected icy particles. Since the colour effect is a fundamental parameter in

remote observations, the whole study has to be done for at least three wavelengths between ultraviolet and infrared to be compared to the remote observations.

4.2. Open questions

Questions related to the formation and evolution of ices in interstellar dust clouds, on cometary dust particles, and on regoliths, are still open. Of major importance is the knowledge of the structure of the ice, which may be amorphous or crystalline (cubic or hexagonal).

A precise knowledge of the nature (and thus the origin) of cometary dust particles in the inner coma (distance to the nucleus below about 2000 km) is still completely missing. It is not expected to obtain some significant in-situ information before the Rosetta rendezvous mission in the next decade.

In the future systematic observations of bright comets have to be pursued. However, objects as bright and extended as the coma of comet Hale-Bopp may only appear once or twice per century. Laboratory measurements performed on at least 3 wavelengths should allow a precise characterization of the wavelength dependence for fluffy and compact particles. It will be of major interest to study the evolution of the light scattering properties during the condensation or sublimation of ices on submicron sized dust grains (cosmic grains), micron sized grains (cometary dust), aggregates with different packing densities and sizes (cometary dust aggregates), and regoliths of high porosity (cometary nuclei, asteroids).

5. Icy particles in the atmosphere

5.1. Formation processes

The atmosphere provides a great variety of iced particles called ice hydrometeors: elementary crystals, snowflakes, graupels and hailstones. Moreover, as dew is produced by diffusion of water vapour on cold surfaces and objects so

rim (also called hoarfrost) is formed at sufficiently low surface temperatures. Ice hydrometeors are mostly characteristic of the troposphere, though in the stratosphere, in correspondence of the polar regions, Polar Stratospheric Clouds (PSC) can be formed and are at least partially composed of crystalline water ice. The ice hydrometeor formation can essentially be ascribed to two processes: diffusion of water vapour on a nucleus or a frozen droplet (with different nucleation mechanisms) and accretion of supercooled droplets on an ice substrate or an embryo. We can have a sequence of the two processes when an ice crystal grown by diffusion can capture supercooled droplets (mostly near to its rim) and freeze them immediately; this sequence is called riming and the hydrometeors form “rimed hydrometeors”.

As for the great variety of forms that the elementary crystals can assume (two examples are shown in Fig. 6) there is a clear indication of the relationship with both supersaturation and temperature from the earlier work of Nakaya and Terada (1935). In Fig. 7 the graph shows the regions corresponding to the different shapes related to the two parameters, through the different growth velocity of the *a* or *c*-axis of hexagonal ice (after Hallett and Mason, 1958). A number of questions remain unsolved and efforts are currently being made to model the process of diffusion of water molecules on the surface of the ice already formed, once they have reached it. The accretional growth of ice, characteristic of graupels and hailstones, has been the subject of research of few but very active research groups, after the relationship had been established for the limit between wet growth (the growth when the latent heat generated in the phase transition on impact cannot all be dissipated to the outside air and inside of the hailstone by conduction and convection and surface temperature of 0°C) and dry growth (when it can be dissipated and the surface temperature of the stone remains below 0°C). The relationship proposed by Schumann (1938) and better defined by Ludlam (1958) can be considered the starting point of hail studies. A subsequent milestone is the

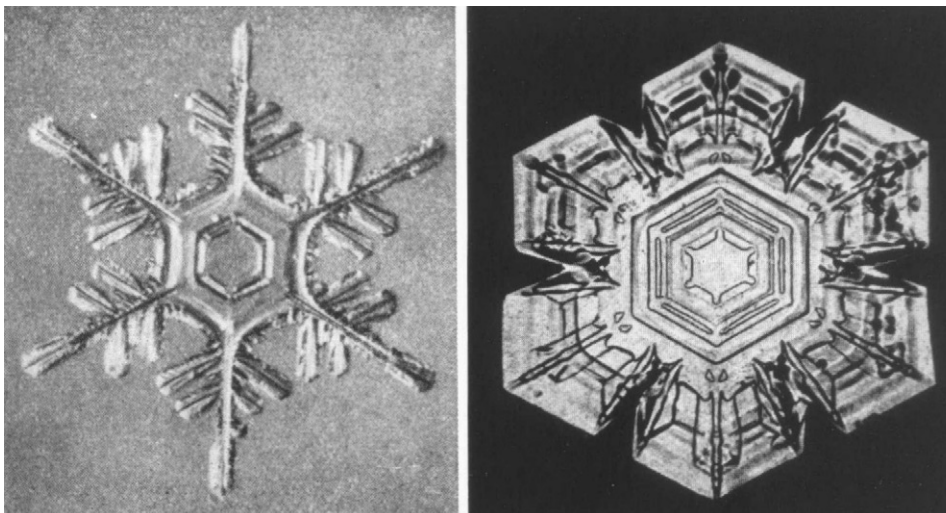


Fig. 6. Two examples of planar ice crystals.

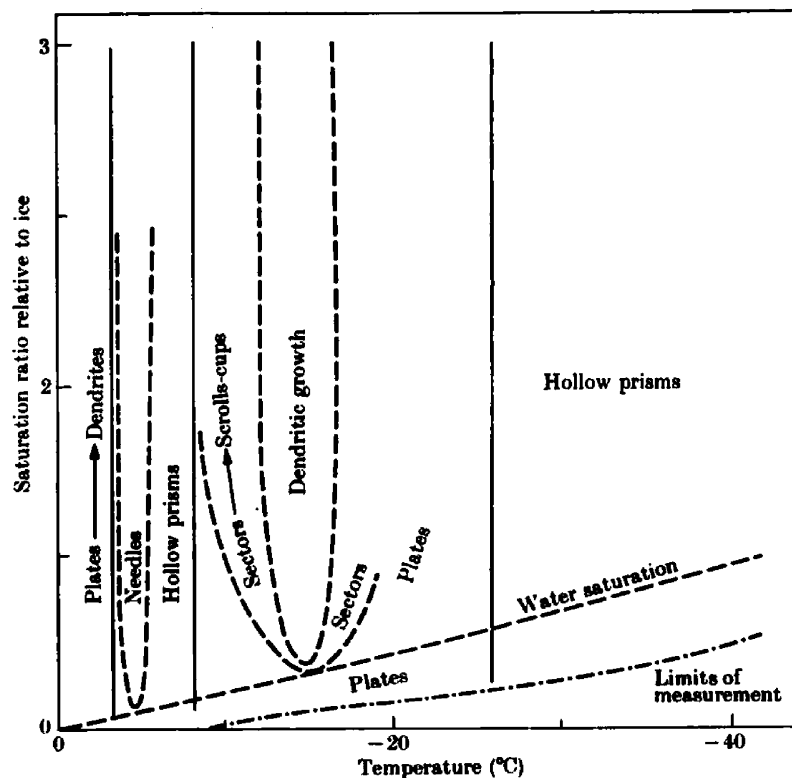


Fig. 7. The growth habits of ice crystals in relation to the temperature and supersaturation of the environment as observed by Hallett and Mason (1958).

discovery by List (1959) that inside the wet growth case we may have also spongy growth, in which the liquid water content of the parent cloud is so high that liquid water can be included inside the hailstone structure itself. Shedding in the wake may also occur at high liquid water contents.

In the following decades relationships have been established between the local density of accreted ice and the growth conditions (Macklin, 1962; Prodi, 1970; Levi et al., 1991; Prodi et al., 1991). The crystallographic properties of the ice grains in the different hailstone layers (their size, length, width, *c*-axis orientation) have also been related to the growth conditions (Prodi and Levi, 1978; Prodi et al., 1982). The morphology of the deposits (opaque or transparent appearance of ice due to the air bubble inclusion, the radial lines of large bubbles, the lobe structure different in the case of dry and wet growth) has also been investigated (e.g. Prodi and Levi, 1980) leading to interesting conclusions on the different role of the Mackin's and Stokes' parameters.

It is also worth mentioning that what is investigated for hailstone growth can have important applications to aircraft icing (for its detection and avoidance) or to icing on structures (electric cables for electricity transport, parts of a ship for sea ice accretion etc).

5.2. Role in climate and chemistry

Particles play an important role in the Earth's climate system and atmospheric chemistry. For example, cirrus clouds,

sometimes originating from aircraft contrails, reflect solar radiation toward space, reducing radiative heating underneath and/or trapping terrestrial infrared radiation, increasing the green-house effect which affects the Earth's radiative budget very substantially (Liou, 1986; Fahey et al., 1999; Ramaswamy et al., 2001). Also, polar stratospheric cloud (PSC) particles trigger chlorine activation via heterogeneous chemistry which results in the dramatic stratospheric ozone depletion in polar regions, the so called "ozone hole" over Antarctica (WMO, 1992; Farman et al., 1985; Solomon et al., 1986). Our attention will be focused here on cirrus clouds and on PSCs, both composed principally of H₂O in crystalline or liquid phases. Water vapour dominates radiative heating in the cloud-free upper troposphere-lower stratosphere region where these clouds are forming, complicating evaluations of the net impact on the radiative budget when these particles are present. Moreover, the formation and evolution of these atmospheric particles is far from being understood, and they remain the major source of uncertainty in radiative and chemical models. Furthermore, these particles are predominantly observed by optical instruments. However, the lack of precise knowledge on their optical properties, shape and composition makes the analysis of these optical measurements uncertain. For example, frequent ground-based lidar measurements provide information on backscattering properties of these particles but reliable retrievals of mean size (or surface) and number density of particles, and determination of their physical phase (solid, liquid or a mixed-phase) remain a challenge.

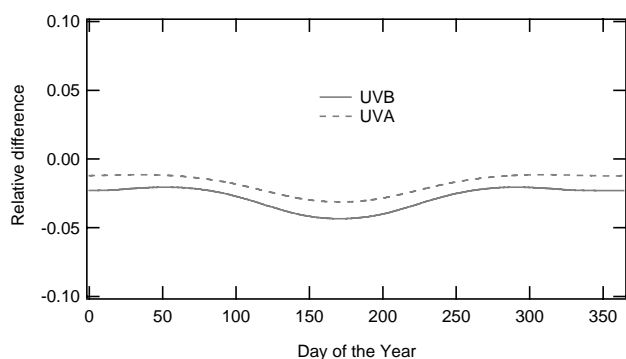


Fig. 8. Relative effect of cirrus cloud optical properties on the seasonal daily mean UVA and UVB calculated for the latitude 40°N . A value of the Henyey–Greenstein scattering phase function coefficient of 0.9 instead of 0.8 reduces UVA and UVB received at ground by 1 to 4% with a seasonal effect. Optical thickness of the cirrus: 0.2 at $1\ \mu\text{m}$, altitude of 10 km.

Cirrus clouds appear in the upper-troposphere-lower-stratosphere region. They are usually optically thin and even invisible (subvisible, optical thickness < 0.03 , Sassen et al., 1989) for a ground-based observer (Goldfarb et al., 2001). They are made of water ice, but recent observations and models show important uncertainties for their formation mechanism: homogeneous freezing of supercooled aerosols or heterogeneous ice nucleation.

Because their frequency of occurrence and optical properties are poorly known, direct and indirect impacts on radiative forcing are not well quantified by radiative transfer and photochemical models (Anderson et al., 1995). Fig. 8 shows results of radiative transfer calculations of the relative effect of cirrus clouds optical properties on the seasonal daily mean UVA and UVB radiations at the latitude 40°N at ground level for one year. Details of the model, extended here in the UV, can be found in Sarkissian et al. (1995). Changing the cirrus cloud particle-scattering phase function affects by 1–4.5% UVA and UVB radiation at ground level with seasonal effect indicating that an accurate evaluation of the cirrus climate forcing can only be achieved if their optical properties are well characterized, as mentioned in EC Report (2001).

PSCs form predominantly in winter in polar regions. They are divided into three classes. Type II PSC are ice particles. PSC type Ia particles are solid nitric acid trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$) and PSC type Ib particles are liquid ternary solutions (H_2SO_4 , HNO_3 , H_2O). A large body of PSC observations are well outside this simple classification, suggesting a much wider spectrum of particle types. The temperature and the evolution of the temperature are critical parameters in determining the type of PSC formed. The role of PSCs on the polar photochemistry and the resulting ozone depletion is determinant for two reasons. First, they are responsible for activation of ozone-destroying chlorine radicals through their well-known heterogeneous chemistry which depends on their size and surface area (WMO, 1992). Secondly, it has been speculated that they can affect the photochemistry

through their scattering properties, enhancing the amount of sunlight available for photolytic processes at the altitude of the PSC layers. Optical properties of PSC particles must be accurately characterized to enable us to retrieve with a good degree of confidence their size and their surface area and to calculate their radiative effects.

Cirrus clouds and PSC particles are now observed on regular basis in the framework of European and international projects. Most recognized instruments developed for their observation are ground-based lidar, satellite-borne occultation spectrometers, balloon-borne occultation spectrometers, balloon-borne backscatter sondes and aerosol counters, and twilight balloon-borne photometers scanning in an horizontal plane (EC Report, 2001). Measured optical parameters such as the back-scattering coefficient, depolarization coefficient, extinction coefficient, number density and scattering phase function are difficult to interpret using more than one of these parameters because (i) of the difficulty to make simultaneous and co-located measurements with different instruments, (ii) of the large inhomogeneity of observed clouds (iii) the air is continuously mixed and (iv) of the differences in the wavelength of the measurements. The analysis of most measurements is based on the Mie theory and on a number of assumptions which cannot be fully tested because of the lack of extensive laboratory measurements of particles mimicking cirrus or PSCs.

5.3. Open questions

Given this status of tropospheric ice research in the present context two main issues can be discerned:

- (i) How can the great amount of knowledge gained on atmospheric icy particles guide us in constructing scenarios of icing in the whole universe? In other words, are the processes encountered in the atmosphere also frequent during cosmic ice formation, and which are the most probable situations (see Fig. 2)?
- (ii) The second issue is related to the usefulness of microgravity conditions in both atmospheric and cosmic ice investigations. Microgravity can help investigations of both, growth of ice crystals by diffusion (they can remain suspended for longer periods in more regular undeformed water vapour fields) and by accretion (we can experience different conditions of relative velocities of embryos and supercooled droplets than those experienced in gravity).

6. Microgravity research

6.1. Crystalline and amorphous material growth on Earth and in space

Crystallization entails two processes: the transport of mass (growth units: molecules, ions, atoms, etc) and/or heat to

the crystal surface, followed by the incorporation of growth units into the crystal structure. The slower of these two processes—transport and kinetics—in a given case controls the crystal growth. While crystallization kinetics, which involves interactions between matter on the atomic scale, is independent of gravity, heat and mass transport is affected by its presence or absence. The movement of mass and heat towards the growing crystal may be diffusive, or may involve bulk fluid flow: convection. One of the most important physical mechanisms that produce convective flow are density differences in different regions of a fluid. Such density differences arise naturally during crystal growth, whether from solution, melt, or vapour, as the growing crystal tends to produce a zone around itself of material of different constitution or temperature compared to that of the bulk. A denser region lying above a less dense region in a gravitational field is potentially unstable, and can produce buoyancy-driven (Rayleigh–Bénard) convection in the fluid. Moreover, the growing crystal will almost certainly have different density to the fluid in which it is immersed. If it is free to move in a gravitational field it will sediment to the bottom of its container, and this too will produce convective movement of fluid. Buoyancy and sedimentation, processes that depend on density differences, are suppressed in the absence of gravity, and for this reason crystallization in microgravity is different from that on Earth. Convection provides more rapid transport than diffusion, and may be space and time dependent, and under such conditions it is more probable that defects are introduced into a crystal lattice. As the aim of much crystal growth is that the lattice be as near perfect as possible, convection may be seen as deleterious for growing crystals under transport control with perfect lattices. Hence the rationale of microgravity crystal-growth research is to provide a diffusive, rather than a convective, growth environment for transport-controlled growth (Garcia-Ruiz et al., 2001a; Giegé et al., 1995).

In the last 25 years crystallization experiments have been conducted in microgravity on alloys, ceramics, proteins, semiconductors, and other materials. In conducting such experiments, it is important to realize that terrestrial crystallization techniques cannot simply be transferred to microgravity; one must concern oneself with the basic physics involved (Space Studies Board, 1995, 2000). For example, surface-tension forces are independent of gravity, hence surface-tension-driven (Bénard–Marangoni) convection, usually important on Earth only in thin layers of fluid with a free surface, becomes the overriding convective mechanism in space upon the suppression of its buoyancy-driven counterpart, if the experimental fluid is allowed a free surface. Moreover, orbiting laboratories provide reduced gravity, but not weightlessness. Residual accelerations and g-jitters arising from crew activities, other experiments, and upper-atmosphere drag mean that even true microgravity—a millionth of Earth surface gravity—is difficult to achieve in manned space missions. On board the International Space Station, a fluctuating gravity level of between 10^{-5} and

10^{-2} g is usual (Hamacher, 1998). Under these conditions, convection is reduced but not eliminated, and for some potential experiments such gravity levels may still be too high to be able to perform the best science (Carotenuto et al., 2002). Thus the crystallization technique must be carefully optimized, bearing in mind the fundamental physics involved to take advantage of microgravity conditions.

In experiments in which such an optimization process has been followed, microgravity research can provide a valuable contribution to our knowledge of how different materials crystallize. For example, in protein crystallization, the use of counterdiffusion crystallization techniques together with the diffusive microgravity environment have allowed the visualization of the depletion zone around a growing crystal (Otalora et al., 2001) (Fig. 9) and the observation of a supersaturation wave travelling along a crystallization chamber (Garcia-Ruiz et al., 2001b). The protein crystals obtained in such experiments are among the most perfect obtained to date, and have allowed sub-Å resolution of the protein structure (Sauter et al., 2001).

While single-crystal growth in microgravity is affected by changes in transport, so too are solidification processes involving multiple crystals, where segregation and sedimentation effects can lead to macroscopic texture changes (Seibert et al., 2001).

This is so, for example, in alloy solidification, in which microstructure formation is a major problem, and microgravity research has helped to understand the mechanisms involved. Amorphous solids—glasses—have also been grown in microgravity, and their structures too may be affected through different transport conditions. This is also true of very open materials, whether polycrystalline or amorphous, which are not compacted in microgravity as they are in a larger gravitational field.

While microgravity directly affects fluid physics, in the case of crystal growth, the gravity level only indirectly affects the crystallization process by changing the fluid environment bounding a growing crystal. Nevertheless, it is fair to say that at this point—after approximately a quarter century of research performed in orbiting laboratories—microgravity crystal growth experiments have not had the same impact on fundamental science in the field as have fluid science experiments in their domain (Space Studies Board, 1995, 2000). With more rigorous controls and better experimental protocols, this situation is now changing, and in the future experiments performed in microgravity must be able to provide useful information on the fundamental science involved. In the case of water ice, there is potentially much of interest to be learned in microgravity experiments, both on crystalline and on amorphous ice. The possibility of altering the transport regime affects morphology—ice crystal morphology depends strongly on temperature (see Figs. 2 and 6)—and will provide very useful information on the fundamental science involved.

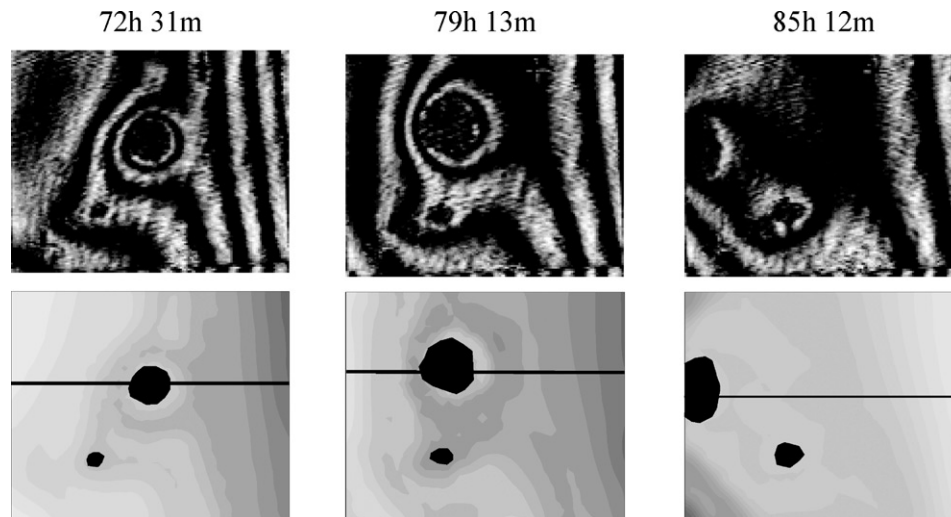


Fig. 9. The depletion zones around growing ferritin protein crystals in microgravity. The figure shows images of two growing crystals at three successive times during the experiment. The upper images are interferograms, and the lower ones are concentration maps (darker grey is more concentrated) computed from the interferometric data. The smaller crystal was growing on the wall of the chamber, so it appears fixed in the images, while the larger one was floating free in the protein solution filling the chamber; it moves across the field of view from right to left. The microgravity environment during this Space Shuttle mission was relatively noisy. This can be seen in the concentration maps; the depletion zone clearly visible around the larger crystal in the first map is distorted in the second, and almost completely absent in the third.

6.2. Ice and regolith studies using microgravity facilities

Measurements on ice and refractory surfaces, as well as measurements on very fluffy particles, can be performed in a ground-based laboratory. On the other hand, measurements on clouds of particles require reduced gravity conditions, as already shown with the PROGRA² experiment (Worms et al., 1999). Besides, measurements on realistic aggregates, formed under ballistic aggregation, require long duration microgravity conditions, as shown with the COsmic Dust AGgregation experiments, CODAG experiments (Blum et al., 2000; Blum et al., 2002; Levasseur-Regourd et al., 2001). In a cloud of micrometer sized SiO₂ particles was dispersed in a rarefied gas atmosphere. Due to the absence of gravity the dust grains are subjected to Brownian motion only. This irregular thermal motion leads to ballistic low-velocity collisions (typical collision velocities are $< 10^{-3} \text{ m s}^{-1}$) and thus sticking between the dust grains. This simulation of the earliest protoplanetary aggregation process showed that fractal aggregates with extremely open structure can form (see Section 3).

Aggregates have to agglomerate in loose structures, to form cometary nuclei. Fluffy aggregates seem to be observed in cometary comae (Greenberg and Li, 1999; Hadamcik and Levasseur-Regourd, 2003). Are these aggregates, after condensation and sublimation of ices the same as when incorporated in the nucleus? Whole-coma polarimetric studies of more than twenty comets have allowed us to define three classes of comets, see Section 4 (Levasseur-Regourd et al., 1996; Hadamcik et al., 1997). Can these observed different physical properties be linked to the region of formation of

the different classes? These open questions need some laboratory work to provide unambiguous answers.

The polarimetric phase curves measured with the PROGRA² instrument in reduced gravity (in the CNES dedicated aircraft) and in ground-based conditions have shown that the polarization of the light scattered by dust particles is a sensitive diagnostic to structural differences in particles. About 70 samples were studied with different parameters such as size of grains (individual or component in aggregates), size of aggregates, refractive index and the packing density of the aggregates (Worms et al., 1999, 2000; Hadamcik et al., 2002a, b; Renard et al., 2002).

Compact particles or relatively dense aggregates were studied in reduced gravity. Highly fluffy aggregates have, up to now, mainly been studied in ground-based conditions when lifted by an air draught, although the problem of segregation by density remains. The short duration aircraft reduced gravity is generally not long enough to regenerate the aggregates that are flattened by the acceleration phase that occurs before (and after) each microgravity period. The levitating particles are thus different to the original ones.

To study icy particles, some preliminary laboratory measurements are necessary to determine i.e. the times scales and to have a first approach of what is expected in terms of light scattering. Two complementary instruments are under study. One of them will allow monitoring the evolution of polarization when ices condense on deposited dust particles (of different materials). The vial is cooled by liquid nitrogen, while the pressure and the vapour pressure are controlled.

With the second instrument under study, ice crystals at low temperatures (obtained by liquid nitrogen and eventu-

ally later by liquid helium) will condense on levitating fluffy aggregates. The light scattering by lifted fluffy dust is currently studied by the PROGRA² experiment but the condensation of ices on the dust particles makes them denser and microgravity is thus necessary for this study, mainly when low pressure is applied. A first step will be the study of condensation of ices on slowly falling particles in a cold gas flow. The time scales to obtain condensation are still open questions for that experiment. Nevertheless, depending on the time scales, aircraft parabolic flights can be a second step. If aggregation processes are expected, long duration microgravity is also necessary.

7. Future perspectives and experiments on the ISS

There are currently no EU, national or internationally funded projects focused directly on the physical and chemical properties of molecular ices formed under microgravity conditions. A previous study of water-ice under microgravity conditions has been performed on Skylab in 1973 (Otto and Lacy, 1973). The Japanese Society for the Promotion of Science, NASDA and the Japanese Space Forum are funding research on the effects of gravity on the growth of ice crystals in thin cells from the solution phase (Nagashima and Furukawa, 2000).

The planned Interactions in Cosmic and Atmospheric Particle Systems (ICAPS) facility (see Fig. 10) on board the International Space Station (ISS) is one ESA funded project (<http://www.icaps.org>), that could offer us the prospect to work with icy particles in microgravity. Its objectives are to characterize the interaction physics of small solid and liquid particles with an ambient gaseous atmosphere, with electromagnetic radiation, and with other particles in their vicinity. The central research topics highlighted on this facility include physics of protoplanetary disks, aerosol and haze physics, regoliths, and light scattering in particulate media.

The experimental programme includes investigations of aggregation, regolith, aggregate collision, as well as cloud experiments. In its current configuration ICAPS is not suitable for ice studies, which require cryogenic and UHV (ultra-high vacuum) facilities. With the ICAPS facility, the lowest attainable temperatures are expected to be around 250 K: a few experiments are therefore possible focusing on icy regoliths, grains and aggregates, coated with I_{HSW} or I_{h} . Furthermore the pressure in the ICAPS facility will only reach 10^{-1} Pa (10^{-3} mbar), suitable for recreating atmospheric conditions, but quite different to the ambient pressure in space environments. ICAPS also focuses on physical not chemical behaviour, and is therefore ill-equipped to look at chemical reactions. As a first step however, this experiment will allow us to study, unimpeded, the physical behaviour and attributes of icy grains, and compare in vacuum, microgravity results with those obtained for e.g. in suspended air flows of small particles. A second interesting step would be to modify the temperature of the experiment from 250 to 100 K, a region in which amorphous rather than crystalline ices could be obtained. Finally, a more difficult step is to modify the experiment to work at 10 K and 10^{-8} Pa (10^{-10} mbar), so that many different space environments can be simulated.

Experiments concerning the agglomeration of *refractory* dust can in general be performed in the laboratory. However, some experiments require the absence of gravity, particularly in the cases where very low velocities are needed (which are otherwise overwhelmed by gravitational settling) or where extremely fragile agglomerates are studied (which may collapse under their weight in the terrestrial laboratory). When icy layers are added to dust particles their mass can increase significantly, leading to sedimentation. However, in advance of utilizing an expensive platform such as the ISS for long-duration experiments, all available microgravity platforms, from short-duration drop towers to parabolic flights, and all ground based laboratory techniques such as

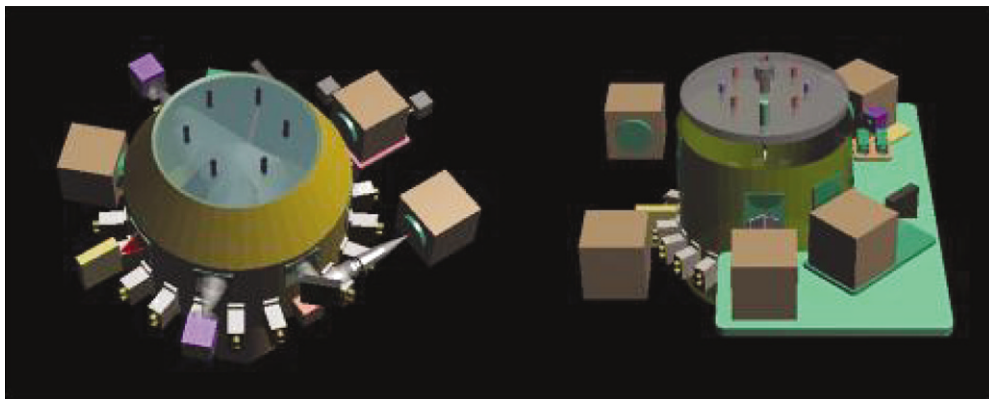


Fig. 10. The ICAPS experiment. The ICAPS experiment, to be flown on the ISS in 2007/8, is currently envisaged to have two experiment chambers. They will be used to study aggregation of small dust particles, and formation of regolith. Equipped to reach pressures of 10^{-3} mbar and operational from ambient temperatures (around 20°C) to 250 K, ICAPS could be used to study a limited range of interactions of icy particles and icy aerosols (see text for details). Courtesy: Kaiser Threde and Nubila.

random positioning machines, particle suspension in traps, air-flow or liquid, and magnetic levitation should be (if possible) utilized for this research field. Of course not all methods are suitable for research in this field, and certain methods, such as particle suspension, which simulate well the interaction between icy particles and the air (gas) for atmospheric science studies are not well suited for recreating icy particle behaviour in low density space environments. Technology can limit certain experiments from being used in random positioning machines, or being placed in or near

high magnetic or electric fields. Drop towers, parabolic flights and sounding rocket flights offer an excellent first step towards disseminating particle behaviour in reduced gravity conditions, but the relatively short duration of such experiments (from a few seconds to a few minutes) is usually insufficient to both grow, observe and react icy particles before sedimentation, gravitational forces or convection interactions set-in. The ISS offers us a unique opportunity to study both the physics and chemistry of icy particles in long-duration microgravity environments.

Table 1

Summary of first generation microgravity experiments on ices, and associated reduced gravity and ground-based studies

Scientific question	Ice phase(s) involved	Pressure/temperature range	Gravitational conditions	Analysis techniques
What is the structure of amorphous ice formed from vapour phase on cold substrate at less than 1 g? ^a	I_{ASW}	$< 10^{-7}$ Pa < 120 K	Microgravity—ISS	<ul style="list-style-type: none"> • Porosity measurements with He–Ne laser • Mass measurements with quartz crystal microbalance (QCM) • FTIR (Fourier transform infrared) transmission spectroscopy/reflection spectroscopy
(With structure we mean the geometrical configuration of the water molecules at atomic scale)			Reduced gravity—parabolic flight ^a	<ul style="list-style-type: none"> • Porosity measurements with He–Ne laser • Mass measurements with quartz crystal microbalance (QCM) (reduced gravity duration too short for other growth + analysis techniques)
			Ground based-laboratory	<ul style="list-style-type: none"> • As per microgravity • Sample mounted horizontally and vertically with deposition from above, below and normal to surface
What is the structure of icy particles formed from vapour phase and liquid phase at less than 1 g?	I_{ASW} I_c I_{HSW} Super-cooled	Ambient (10^5 Pa) to $< 10^{-7}$ Pa 10–273 K	Microgravity—ISS	<ul style="list-style-type: none"> • Porosity measurements with He–Ne laser • Mass measurements with quartz crystal microbalance (QCM) • FTIR (Fourier transform infrared) transmission spectroscopy/reflection spectroscopy • Cavity ringdown spectroscopy • X-ray diffraction (powder-like) • Light scattering analysis • Light scattering analysis
How do icy particles aggregate? ^b			Reduced gravity—parabolic flight & drop tower	<ul style="list-style-type: none"> • Particle suspension in airflow or magnetic/ion traps can be used for LIMITED analysis of physical behaviour before particles sediment, but ONLY in the case where pressures are close to ambient, and temperatures resemble atmospheric conditions
			Ground based-laboratory	<ul style="list-style-type: none"> • Light scattering analysis • CCD camera/video recording • Mass spectroscopy • Light scattering analysis • CCD camera/video recording

Table 1 (Continued)

Scientific question	Ice phase(s) involved	Pressure/temperature range	Gravitational conditions	Analysis techniques
How does the chemical behaviour of icy particles differ from that of thin film surfaces? ^c	I_{ASW} I_c I_{HSW}	Ambient (10^5 Pa) to $< 10^{-7}$ Pa	Microgravity—ISS	<ul style="list-style-type: none"> • FTIR (Fourier Transform Infrared) transmission spectroscopy/reflection spectroscopy • Mass spectrometry • Cavity ringdown spectroscopy • Light scattering analysis • Particle suspension in airflow or magnetic/ion traps can be used for LIMITED analysis of chemical behaviour under atmospheric pressure/temperature conditions only (formation + reaction time = longer than particle sedimentation time)
	Super-cooled	10–273 K	Ground based-laboratory	

^aFor this scientific driver there are no advantages in moving from parabolic flight to sounding rocket experiments, as reduced gravity timescales are still insufficient for additional analysis techniques. Random positioning, up-flow and magnetic levitation techniques are also not convivial to I_{ASW} growth and analysis techniques.

^bFor this scientific driver there are no advantages in conducting ground based experiments as the more massive icy particles sediment out much faster than the dust seedlings/aerosols on which they are grown, resulting in aggregation between only the smallest particles which is not representative of the true atmospheric or astronomical conditions.

^cFor this scientific driver there are no advantages in using parabolic flight or drop tower experiments as reduced gravity timescales are still insufficient to form and react and analyse the icy particles.

However, to fully investigate the physics and chemistry of icy particles in microgravity environments an alternative set of analysis instrumentation is required, none of which are currently available on other ISS experiments, e.g. X-ray diffraction (XRD), mass spectrometry (MS) or infrared (IR) spectroscopy. As an ESA Topical Team we are currently evaluating the specific adjustments that are necessary to existing ISS experiments, and the design of a novel stand-alone experiment that could be equipped with a cryogenic facility (to allow measurements at 10 K), an ultra-high-vacuum (UHV) system and additional instrumentation for physical and chemical analysis. Such an infrastructure on the ISS, could be widely used by both the astronomy and atmospheric science communities, as well as for basic physics and chemistry research, providing answers to some of the fundamental questions concerning the formation and evolution of our solar system.

One basic objective of a dedicated ice-microgravity experiment would be to investigate the morphologies of amorphous ices obtained when the ice is grown from both vapour and liquid phases under microgravity conditions, see Table 1.

Simple mass measurements, made in situ, would allow us to determine the morphology of the ice particles, and their aggregates, and a comparison of these morphologies with the structures of amorphous thin films grown in the laboratory or generated theoretically.

A second major objective would be to follow the aggregation of icy grains into bigger structures (i.e. flakes) and the

behaviour of such particles after sublimation of the ices; e.g. if we take ice-coated dust grains, aggregate them together, and heat up slowly (as in a sun-passage of a comet): does the ice melt and thus force the aggregate to shrink together to form a dense clump? Or does the ice sinter together forming an even more consolidated ice-dust aggregate? Or does the ice evaporate and drag the dust grains along by aerodynamic friction? Or does the ice evaporate and leave a dust aggregate with basically unaltered morphology?

This is representative of the physical processes that begin in the interstellar medium progressing into the protosolar nebula, and later in cometary nuclei, cometary comae or interplanetary media. Long duration microgravity conditions are essential to follow these changes, to ensure one single dust population is observed continuously, and to avoid any sedimentation effects as particles aggregate, or as ices are accreted onto and sublimated from the grains. It will also be vital to have the flexibility to repeat the experiment in cycles, in order to compare the results.

Experiments on board the Space Station will allow us to study the evolution of the dust light scattering properties during the condensation or sublimation of ices on sub-micron sized dust grains (representative of cosmic grains), micron sized grains (cometary dust) aggregates with different packing densities and sizes (cometary dust aggregates), and regoliths of high-porosity (cometary nuclei, asteroids). As described in Section 3/4 above, such experiments are vital to our dissemination of observations from comets and outer solar system bodies, as well as icy planets and satellites in

our own solar system. Optical monitoring of the formation and evolution of atmospheric particles in a controlled microgravity environment should help to understand the microphysics of these particles and to characterize their optical properties without being hampered by sedimentation and air flow as found in a ground-based laboratory environment. Microgravity is also important in investigating scavenging of particulate and gaseous pollutants by ice hydrometeors in clouds, and this is one aspect of ICAPS. In particular, among the different processes of capture of particles by hydrometeors, Brownian diffusion, electrostatic forces, aerodynamic capture and thermo- and diffusio-phoresis, the latter appear most promising for microgravity investigation.

To summarize, many open questions remain to be answered before we can fully comprehend ice-particle morphologies in different space environments. Laboratory work on low-temperature H₂O ices has shown that a variety of different microscopic amorphous structures are possible. Studies under microgravity conditions will allow us to elucidate the underlying physics governing water-ice formation from the vapour and solid phases. Once formed, the chemical reactions and the physical behaviour of these icy particles will offer us a key insight to many unanswered problems in both astronomy and atmospheric chemistry. A dedicated experiment on the ISS would appeal to a wide range of researchers in a variety of disciplines. More knowledge is required to understand the agglomeration of ice and dust into planetesimals, and to then describe how these assemblies subsequently formed our planets and other small solar system bodies. Formation and evolution of atmospheric icy particles is far from being understood and this is a dominant source of uncertainty for radiative and chemical models.

The ISS offers us a unique opportunity to conduct long-duration microgravity experiments on icy particles, applicable in a vast range of interdisciplinary fields, and is certain to greatly assist us in addressing many unanswered questions in these areas. In particular it will help us to understand and identify the key chemical and physical processes associated with ices in the formation and evolution of our solar system, Earth's atmosphere and climate.

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