# PHYSICO-CHEMISTRY OF COMETS: MODELS AND LABORATORY EXPERIMENTS

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**Abstract.** Until cometary matter can be studied in-situ or cometary samples are brought back to Earth for analysis, theoretical models and laboratory studies remain a crucial tool for revealing the nature of cometary matter. Constraints on the nature of the primordial material available for incorporation into comets and other solar system material comes from analysis of data from space-based and ground-based observatories. The structure of the nuclear ice component, which may have coexisting amorphous/crystalline phases and include clathrates and other trapped guest molecules, strongly influences the cometary outgassing properties. This paper reviews laboratory work on ice and carbonaceous compounds and discusses their significance for cometary chemistry. Special emphasis will be given to studies on the thermal processing of ices and their implications for the structure changes and subsequent release of volatiles. We also describe the preliminary results of a model of nuclear outgassing, and discuss how such models can be used to infer the chemical structure of the nuclear ices. Furthermore, we confront cometary data with the analysis of carbonaceous meteorites. Recent laboratory results on volatile compounds and the macromolecular structure of carbonaceous meteorites allow us to investigate the link of small bodies in the Solar System. Until ROSETTA will land on comet Wirtanen and study directly the nuclear composition, laboratory measurements of ice and refractory analogs will - together with the analysis of meteorites – significantly improve our knowledge on the origin and structure of comets.

**Keywords:** Comet C/1995 O1 Hale–Bopp, comets, laboratory studies, physico-chemsitry

## 1. Introduction

The nucleus of a comet is a conglomeration of ices, refractory and organic compounds. Comets have been formed in the outer solar system, beyond the orbit of Jupiter and are therefore relatively pristine. Revealing their composition provides clues to the formation of our solar system. By comparing the distribution and abundances of species observed on interstellar icy grains with cometary observations the amount of processing those objects have undergone during solar system formation can be estimated.

The composition of comets has been recently reviewed (Altwegg et al., 1999; Crovisier and Bockelée-Morvan, 1999; Irvine et al., 2000; Ehrenfreund and Charnley, 2000; Charnley et al., 2002). The substantial number of bright comets in recent years allowed high resolution measurements and provides stronger evidence for

chemical differentiation amongst the comet population. The depletion of short carbon chains was first demonstrated by A'Hearn et al. (1995) in short-period comets. More recently, ethane has also been found to be depleted in the short period comet Giacobini–Zinner (Mumma et al., 2000). Comet S4 LINEAR shows depletions in $CH_3OH$ and CO (Bockelée-Morvan et al., 2001; Mumma et al., 2001a), whereas Comet Lee has a normal $CH_3OH$ abundance but CO is strongly depleted (Biver et al., 2000; Mumma et al., 2001b). This differentiation places constraints on the chemical history of the organic material in those comets and on their place of origin.

Cometary ices are predominantly (more than 50%) water ice, but by now more than 25 other small molecules have been identified. Their abundances relative to water molecules range from $\sim$10% for CO (there is also usually a significant nonnuclear contribution from distributed sources in the coma, see Section 5) down to 0.01%, which is at present the lowest abundance detected. The inventory of cometary species is certainly not yet complete for molecules with abundances less than 1%. Many small reactive molecules are detected: $H_2O$, $CO_2$, $H_2CO$, $NH_3$, HCN, $CH_3CN$, $C_2H_2$, HNCO and $H_2S$. More complex species observed are $CH_3OH$, $CH_3CHO$, $HCOOCH_3$, and $NH_2CHO$ which bears some resemblance to glycine, $NH_2CH_2COOH$. Glycine, the simplest amino acid, has itself not yet been detected, and the present upper detection limit of <0.5% is not very significant compared to other species. Note that these molecular abundance ratios are obtained from gas phase observations of the coma. The exact relation between coma abundances and the nuclear ice composition is not fully understood, and is discussed in detail in Sections 4–7.

In this review we focus on the icy volatiles and the organic constituents of comets. We summarise the major results obtained over the last few years, with an emphasis on the insights gained from laboratory studies of cometary analogs. For a review of the inorganic refractory component of comets, the reader is referred to Wooden (2002).

## 2. Ice Chemistry in Interstellar Molecular Clouds as Constrained from Laboratory Data

Interstellar clouds collapse to form stars and planetary systems. The infalling cloud matter is processed in different ways according to its proximity to the protostar. In the inner regions of protoplanetary disks, ices are sublimated and grains are subjected to high temperatures, shocks and a strong radiation field. Large scale turbulent mixing of gas and solids rearranges the material within the disk before it is later incorporated into planets and small solar system bodies. Concerning the ice composition of comets, a comparison of outgassing curves from bright comets with present data of cold interstellar clouds provides an important tool to estimate the amount of processing the original cloud material has undergone. Similarities of

abundances for selected species in cometary comae and interstellar clouds are evident (see Table I in Charnley et al., 2002). Most of the data compiled for interstellar regions are taken from high-mass protostars, which follow a different evolution compared to low-mass stars like our sun. Low mass protostars are not yet well studied due to their faint signal, except for the dominant molecules $H_2O$, CO and $CO_2$ (Boogert et al., 2000). The abundances of, e.g., $CH_3OH$ and $NH_3$ are scarce, and certainly in strong contrast to some high mass protostars.

In dense interstellar clouds, atoms and molecules begin to freeze out onto dust particles, forming icy mantles over the underlying silicates and organics (Ehrenfreund and Schutte, 2000). At 10 K only H, D, C, O and N atoms have sufficient mobility to interact on the surfaces of grains. Molecules such as $H_2O$, $NH_3$, or $CH_4$ can be formed by simple exothermic hydrogen addition reactions. The presence of more complex molecules (e.g., $CH_3OH$) can only be explained by surface reactions that are acting on and in the icy mantles (Brown and Charnley, 1990). Water ice is the most abundant ice component formed in icy grain mantles and abundances of other species are therefore scaled relative to $H_2O$ ice. Other species are either trapped in the water ice matrix or are present in distinct layers on the same dust particle. Successive layers of ice are formed when grains travel through star-forming regions which are characterised by different temperatures and density conditions.

In order to identify species and to measure their column densities in space, laboratory experiments, simulating space conditions, are essential (Ehrenfreund and Fraser, 2002). Low temperature infrared spectroscopy is used as an effective method to obtain data of ice analogs for the interstellar medium as well as solar system objects. Temperatures of 10 K and pressures of $<10^{-8}$ mbar used in those laboratory simulations represent conditions prevailing in dense interstellar clouds. 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 $\sim10^7$ years.

Laboratory data allow us to identify the spectroscopic signatures of different grain populations and grains with multi-layer structures in the line of sight toward star-forming regions. Closer to the star only polar ices (dominated by $H_2O$ ice) are present. Polar ices contain besides water ice some CO, $CO_2$, $CH_4$, $NH_3$, $CH_3OH$, and possibly traces of HCOOH and $H_2CO$. Some fraction of those molecules stays trapped and evaporates together with water at $\sim100$ K. In cold regions grains may accrete additional layers of volatiles from the gas phase, such as CO or $N_2$. These ice layers contain very little water ice and are also known as apolar ices. Trace amounts of other species such as OCS, $H_2CO$, HCOOH, $CH_4$, and $OCN^-$ have been observed with the Infrared Space Observatory (ISO) near some protostars. They are characterized by abundances between less than a percent to a few percent relative to water ice (Ehrenfreund and Charnley, 2000; Gibb et al., 2000; Keane et al., 2001). OCS is currently the only sulphur-containing species identified in

interstellar ices, and has an abundance of less than 0.2% relative to water ice (e.g., d'Hendecourt et al., 1996). Little is known about the abundance of the homonuclear molecules $H_2$, $O_2$ and $N_2$. Large amounts of oxygen and nitrogen are unaccounted for in the interstellar medium and the presence of substantial amounts of those species in molecular form has therefore been suggested. Since these molecules are practically infrared inactive only upper limits for $O_2$ and $N_2$ (transitions at 6.45 and 4.28 $\mu$m, respectively) have been reported by Vandenbussche et al. (1999) and Sandford et al. (2001), respectively. Observations with the Submillimeter Wave Astronomy Satellite (SWAS) show practically no molecular oxygen in the gas phase (Goldsmith et al., 2000), which would imply that very little $O_2$ will freeze out on interstellar grains.

A number of laboratory studies have been undertaken of the surface chemistry occurring on interstellar ice analogs. 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). Whether or not such processes are occurring efficiently in space may be tested by observations of isotopically substituted species in the interstellar medium (Charnley et al., 1997, 2002).

The chemistry of icy grains is strongly influenced by the environmental conditions. Thermal processing close to the star leads to motion and structure changes within the ice matrix. Ice segregation of $CO_2$ and $CH_3OH$ has been observed with ISO (Ehrenfreund et al., 1998). Even the intermolecular interaction of these molecules have been traced in the spectra of distant molecular clouds (Dartois et al., 1999a), see Figure 1. 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; (—$CH_2$—O—)$_n$; Schutte et al., 1993). The presence of POM in comets has long been advocated as the explanation for the extended source of $H_2CO$ seen in many comets (see Section 5.1).

Energetic processing of ices due to ultraviolet (UV) irradiation and cosmic rays also drives the complexity of species within the grain mantles (Allamandola et al., 1999; Moore and Hudson, 1998). However, the attenuated UV field in dark clouds will contribute only a limited amount of energy for chemical reactions (Ehrenfreund et al., 2001a). Although laboratory experiments show that a suite of organic molecules is reproduced during UV irradiation of ice mixtures and subsequent warm-up (e.g., Bernstein et al., 1997), it is not clear how efficient this process will proceed in dark clouds. Cosmic rays are a more relevant source for grain mantle alteration (Moore and Hudson, 1998; Cottin et al., 2001a) in dense star-forming cloud cores. These processes may have also altered cometary ices over the

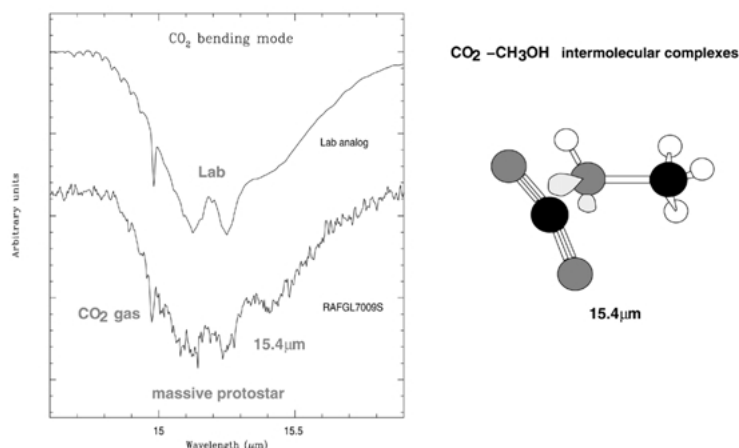## Thermal processing of icy grains in star–forming regions



*Figure 1.* The 15.2 $\mu$m bending mode of $CO_2$ ice has been observed ubiquitously in interstellar space. The origin of its pronounced triple peak, as seen here through the line of sight toward the protostar RAFGL 7009S, was long unknown. Extended laboratory work revealed that this spectroscopic signature can be best reproduced with ice mixtures containing $CO_2$ and $CH_3OH$ in equal proportions (and some water) at elevated temperatures (Ehrenfreund et al., 1998). Whereas the two peaks with roughly equal intensity witness the segregation of $CO_2$ into boundary layers (splitting of the 15.2 $\mu$m $CO_2$ bending mode is only observed in pure $CO_2$ ice), $CO_2/CH_3OH$ complexes are responsible for the shoulder at 15.4 $\mu$m (Dartois et al., 1999a). The sharp feature at 14.98 $\mu$m is due to gas phase $CO_2$.

lifetime of the solar system. However, this processing will be confined to a thin layer on the surface of the comet, which will be rapidly lost upon the comet's first approach toward the sun. Therefore, any evidence of photolysis and/or radiolysis in cometary ices is likely to be a signature of events that occurred before the ice was incorporated into the comet.

No larger species than $CH_3OH$ has been unambiguously identified so far on interstellar grain mantles. The rich infrared spectrum of star-forming regions suggests that some of the larger compounds may be hidden below dominant features of more abundant molecules. In general, however, the abundance of more complex species will be very low (less than 1%) and probably be only detectable with much higher sensitivity than the previous satellites could provide. Methanol, together with ammonia, is a key molecule in reaction pathways leading to further complexity. The abundance of both molecules is strongly varying and/or debated (Dartois et al., 1999b; Lacy et al., 1998; Dartois and d'Hendecourt, 2001; Gibb et al., 2001). New VLT observations confirm the results of Dartois and d'Hendecourt (2001) that $NH_3$ is only present in small abundance of a few percent relative to water ice (Dartois et al., private communication). The low $NH_3$ abundance provides constraints on the formation of more complex species. The formation of larger molecules may be restricted to the gas phase in regions close to massive stars, which produce a
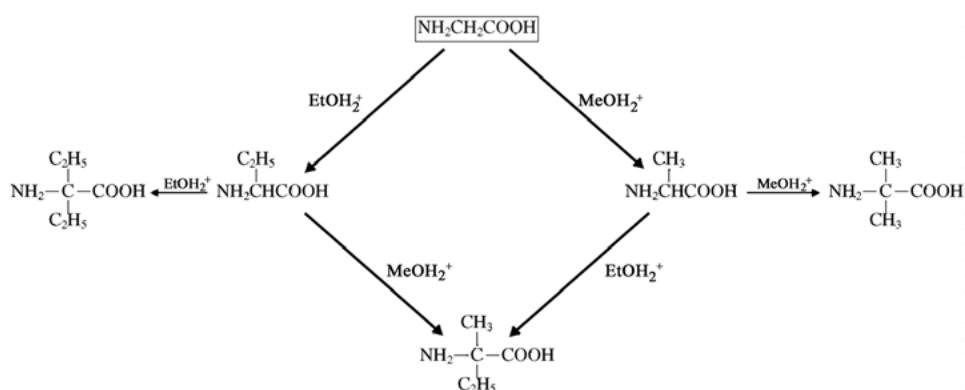
*Figure 2.* Chemical routes to molecular complexity in hot cores. Aminomethanol ($NH_2CH_2OH$) is assumed to evaporate from grain mantles. Proton transfer followed by reaction with formic acid may lead to glycine. Subsequent reactions with protonated alcohols lead to even larger molecules. From Charnley et al. (2001).

large energy input to the surrounding cloud. In these "hot core" regions most of the complex organic molecules, which are currently known, have been identified. It is here that gas-phase reactions of sublimated species are thought to give rise to molecules such as $(CH_3)_2O$ and $HCOOCH_3$, and potentially to heavier "biogenic" species such as (yet unconfirmed) glycine (Charnley et al., 2001), see Figure 2.

## 3. Carbonaceous Dust

The main spectroscopic evidence for carbonaceous material in the interstellar medium are the 220 nm bump in the interstellar extinction curve, attributed to amorphous carbon (Mennella et al., 1998), and the infrared emission features, attributed to aromatic material (e.g., Allamandola et al., 1999). Organic compounds observed or suspected in diffuse clouds are carbon-chains, diamonds and fullerenes (Ehrenfreund and Charnley, 2000).

Astronomical observations suggest that a dominant fraction might be present in aromatic gas phase species polycyclic aromatic hydrocarbons (PAHs), namely up to 15%. The signature of PAHs is observed through their vibrational frequencies in the infrared between 3–15 $\mu$m (Tielens et al., 1999; Allamandola et al., 1999). Two decades of research show strong evidence that PAHs are the most abundant organic molecules present in the interstellar gas in many galactic and extragalactic regions. Free individual PAH molecules, PAH clusters and particles comprised of aromatic (PAH) subunits are believed to be responsible for the overall interstellar emission spectrum.

Most of the C in space (up to 50%) incorporated into carbonaceous dust in the interstellar medium may show considerable diversity. Amorphous carbon (AC), hydrogenated amorphous carbon (HAC), coal, soot, quenched-carbonaceous con-

densates (QCC), diamonds, and other compounds such as complex kerogen-type material have been suggested (e.g., Papoular et al., 1996; Henning and Salama, 1998; Ehrenfreund and Charnley, 2000 and references therein).

Interstellar material – pristine or processed – must make up a substantial part of the nucleus. The composition of the nucleus is in generally inferred from the outgassing of volatiles in the coma. During the flyby of the Giotto spacecraft at comet 1P/Halley the chemical composition of cometary grains has been analyzed in situ by mass spectrometers on board the Vega 1 and 2 spacecraft (Fomenkova, 1999). A large collection of grains was obtained with masses from $5 \times 10^{-17}$ to $5 \times 10^{-12}$ g. The majority of dust grains show a mixed phase of organics and silicates. Only ∼30% of the grains do not contain any organics. CHON particles, containing mainly C, H, O, N atoms are interspersed on the submicron scale with silicate components.

A list of organic compounds in the grains has been compiled from PUMA data (Kissel and Krueger, 1987). The identification of those organics remains, however, speculative due to the limited resolution of the mass spectrometers. In 1994, Moreels et al., claimed the detection of phenantrene by UV spectroscopy in comet Halley. However, no PAHs have been seen in the ISO spectra of C/1995 O1 Hale–Bopp (Crovisier, 1999), which may be due to a larger heliocentric distance. The large amount of aromatic carbonaceous matter in the interstellar medium, suggests that a substantial part of this material must have been incorporated into comets. Cometary outbursts have been attributed to HCN polymers (Rettig et al., 1992) and the existence of POM on cometary particles could be responsible for the presence of the extended source of $H_2CO$ in the coma (Huebner et al., 1989; see Section 5.1 below). The *in situ* measurements taken by future space missions may shed some light on the distribution of complex organics in comets. However, we will have to await a sample return mission to thoroughly study material larger than 500 atomic mass units.

In the meantime, laboratory experiments, which provide important constraints for the composition of solar system material, include the analysis of meteorites. Carbonaceous meteorites, contain about 3% of carbon and show a similar distribution of carbonaceous matter as observed in the interstellar medium. A large amount (80%) of the carbon fraction is incorporated into an insoluble kerogen-type carbonaceous network. The soluble fraction contains mainly PAHs, amino acids and a number of organic acids. The analysis of both fractions, insoluble and soluble, has made strong progress in recent years due to innovative methods (Gardinier et al., 2000; Botta et al., 2001).

We have recently examined pristine pieces of the CI carbonaceous chondrites Orgueil and Ivuna for the presence of amino acids by high performance liquid chromatography (Ehrenfreund et al., 2001b). The amino acid composition is strikingly different compared to the well studied CM carbonaceous chondrites Murchison and Murray. The comparison of chromatograms, shown in Figure 3, indicates that Orgueil and Ivuna must originate from a different parent body. Whereas C and
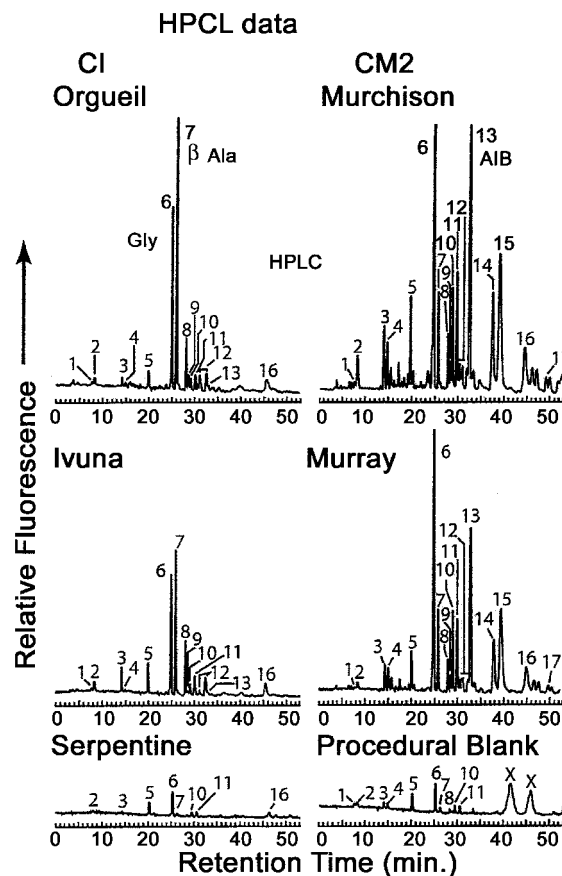
*Figure 3.* The 0 to 53 minute region of the HPLC chromatograms of derivatized extracts from the CI carbonaceous chondrites Orgueil and Ivuna, the CM chondrites Murchison and Murray, and the Serpentine and procedural blanks are shown. Peaks were identified as follows: 1, D-aspartic acid; 2, L-aspartic acid; 3, L-glutamic acid; 4, D-glutamic acid; 5, DL-seranine; 6, glycine; 7, $\beta$-alanine; 8, $\gamma$-ABA; 9, DL-$\beta$-AIB; 10, D-alanine; 11, L-alanine; 12, DL-$\beta$-ABA; 13, AIB; 14, D,L-$\alpha$-ABA; 15, DL-isovaline; 16, L-valine; 17, D-valine; and X, unknown.

G asteroids indicate similar spectral properties as heated Murchison and Murray samples (Hiroi et al., 1993), the current inventory of cometary volatiles would favour an amino acid composition as seen in the CI chondrites Orgueil and Ivuna (Ehrenfreund et al., 2001b). Meteorites are the only extraterrestrial material which is available for the analysis in Earth laboratories with sophisticated instrumentation. Their composition reveals the chemical processes on small bodies in our solar system and gives us crucial information on the large unknown carbon fraction of cosmic material.

## 4. Cometary Comae

When we observe comets, at most wavelengths the nucleus is obscured by the surrounding coma. Although the Giotto and Deep Space 1 missions obtained pictures of the nuclei of comets Halley and Borrelly respectively (Keller et al., 1987; Soderblom et al., 2002a), we must still await the rendezvous of the Rosetta mission with comet Wirtanen before an *in situ* analysis of the nucleus is possible. Hence, in order to accurately interpret observations of the coma in terms of the chemical and physical composition of the nucleus, it is necessary to develop detailed models of the processes which occur in the coma.

We have developed a model of the hydrodynamics and chemistry in the coma, and have used the model to follow the chemistry of HNC, large organics, and deuterated molecules (Rodgers and Charnley, 1998, 2001a,b, 2002). A more detailed discussion of the coma chemistry appears in Charnley et al. (2002), and here we give a very brief summary of our results. Generally, we find that bimolecular reactions in the coma are inefficient at synthesising large amounts of daughter molecules, and we conclude that species such as formic acid, methyl formate, methyl cyanide and cyanoacetylene must have been present in the nucleus of Hale–Bopp. We find that reactions with energy barriers may be overcome by the fast suprathermal H and D atoms produced in the photodissociation of water, but there is no direct evidence that such reactions contribute to specific molecules observed in the coma. We also find that the most likely source of cometary HNC is the degradation of some large organic macromolecule (see Section 5.2 below).

In the following section we review the principal physical and chemical processes occurring in the coma, and we discuss the laboratory experiments which have been (or need to be) undertaken in order to fully understand them.

### 4.1. PHYSICAL PROCESSES IN THE COMA

The chemistry and the physics in the inner coma are strongly coupled, which is why it is necessary to develop combined physical/chemical models of the coma. Photodissociation and photoionisation reactions heat the outflowing gas, and elastic and inelastic collisions redistribute this energy amongst the three principal fluids. Also, in the inner coma inelastic collisions with water and electrons are important in determining the rotational level populations of molecules (e.g., Biver et al., 2000). To date, very few of the appropriate collisional cross-sections have been measured in the laboratory (e.g., Cravens and Körosmezey, 1986; Xie and Mumma, 1992). In the outer coma, the level populations are controlled by fluorescent pumping. Again, laboratory measurements of infrared absorption band strengths are vital to ensure that the observational data can be interpreted accurately. This is particularly important in the case of water, since telluric extinction ensures that direct detection of $H_2O$ via ground-based telescopes is only possible via infrared "hot bands" (Dello Russo et al., 2000).

It has long been appreciated that cometary comae contain a population of fast, suprathermal H atoms produced in the photodissociation of water (Ip, 1983). Due to their small mass these atoms receive most of the excess energy of the reaction, and it is the thermalization of these atoms that is the principal heat source in the inner coma. It is also possible that these atoms can drive chemical reactions with large activation energy barriers (Rodgers and Charnley, 1998). Therefore, it is necessary to know how much of the excess energy of photodissociation reactions is given to the H atom as kinetic energy, and how much results in excitation of the OH radical. Recent experiments have demonstrated that the OH radicals can end up with as much as 75% of the excess energy, and be excited into rotational energy levels as high as $J = 45$ (Dixon et al., 1999; Harich et al., 2000). Thus, earlier models may have overestimated the temperature in the inner coma, and fast H atom reactions may not be as effective as originally thought (Rodgers and Charnley, 2002a).

Finally, cometary X-ray emission was detected for the first time in comet Hyakutake (Lisse et al., 1996). It is now known that the X-rays are produced by the interaction of the solar wind with the cometary gas. Again, laboratory measurements are essential to understand quantitatively the nature of the interaction (e.g., Greenwood et al., 2000; Hasan et al., 2001).

## 4.2. COMA CHEMISTRY

The primary chemical reactions which occur in the coma are the photodissociation of the initial parent molecules. Photodissociation rates appropriate for the solar radiation field were calculated by Huebner et al. (1992) for a large number of molecules and radicals.* However, in some cases experimental data are only available for a very limited number of wavelengths, and the computed cross-sections are based on interpolation and/or estimates. In addition, the discovery of many new organic molecules in Hale–Bopp has shown that more complex molecules are likely to be present in comets. In order to calculate the production rates of molecules from observations of the coma, it is necessary to know the lifetime against photodissociation. Hence, it is essential for measurements of the photodissociation rates of large cometary molecules to be measured in the laboratory (see Jackson et al., these proceedings).

We have recently measured the photodestruction rates of a number of potentially very important cometary and interstellar molecules (Ehrenfreund et al., 2001a). In order to determine lower limits to the appropriate gas-phase rate, or for ices, the molecules are trapped in Argon or water matrices. To date, we have measured formic acid (HCOOH; Ehrenfreund et al., 2001a), amino acids (Ehrenfreund et al., 2001c), and are currently working on nucleobases.

In addition to measuring the total photodestruction rate, it is important to know the reaction products and branching ratios. For example, in principle photodissociation of HNCO could account for the extended HNC source seen in comet Lee

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*  This database is accessible online at `http://www.space.swri.edu/amop`

(Rodgers and Charnley, 2001b). However, laboratory studies suggest that, as expected, the H–N bond is easier to break than the C=O bond and HNC is not produced from HNCO (Okabe, 1970). Knowing the branching ratios is particularly important for deuterated species, since most models assume that the position of the H's and D's in the products are governed by statistical considerations, whereas the limited experimental data appear to show a preference for H rather than D atom ejection (e.g., Zhang and Imre, 1988; Wang et al., 1997).

We have already mentioned that chemical reactions in the coma appear to be unable to form sufficient abundances of the molecules seen in Hale–Bopp. Nevertheless, coma chemistry plays a key role in determining the abundances of ions in the coma. As in interstellar hot cores, the coma chemistry is dominated by a proton cascade, whereby ionised parent species (e.g., $H_2O^+$) react with neutral parents with higher proton affinities, to form ions such as $H_3O^+$, $HCNH^+$, and $NH_4^+$. Many ions were detected by the ion mass spectrometer on the Giotto probe in the coma of comet Halley (e.g., Altwegg et al., 1993), and similar measurements were carried out by the PEPE instrument on Deep Space 1 (Reisenfeld et al., 2002). In order to understand the results of such measurements a detailed model of the ion-molecule chemistry is necessary. In particular, it is essential that the endo- or exo-ergicity for all proton transfer reactions is known (e.g., Rodgers and Charnley, 1998). The latest measurements of the proton affinities for a large number of species were published by Hunter and Lias (1998).*

## 5. Extended Sources of Coma Molecules

In the case of some cometary molecules, in addition to a nuclear (or "direct") source, there also appears to be an additional "extended" source in the coma. The existence of an extended source of formaldehyde was apparent in comet Halley (e.g., Meier et al., 1993). Other molecules now thought to have extended sources in at least one comet include CO, HCN, HNC, and OCS. Long term monitoring of the coma composition of Hale–Bopp demonstrated that the coma abundances (relative to HCN) of $H_2CO$, HNC, and CS increased as this comet approached the sun (Biver et al., 2002). This is evidence that these species are released via the photodegradation of complex organic material, which will only sublimate from the nucleus at small heliocentric distances. In addition, many radicals also exhibit extended sources. This is to be expected if these species are formed via photodissociation of stable closed-shell parents, and in principle observations of 'parent-daughter' pairs can be used to test photochemical models of the coma. However, the nature of the parent molecule for most radicals remains ambiguous, and it remains possible that small carbon chains such as $C_2$ and $C_3$ may also have refractory parents.

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\* See `http://webbook.nist.gov/chemistry`

## 5.1. $H_2CO$

We have previously mentioned the experiments of Schutte et al. (1993), who showed that spontaneous polymerization of $H_2CO$ ices into POM can occur if $NH_3$ is also present and the ices are heated. Based on regular peaks in the mass spectrum of organic refractory material in comet Halley, Huebner (1987) proposed that POM was a key constituent of this material. Mitchell et al. (1989) argued that similar mass spectra would arise from any large molecules rich in C, N, O, and H, which means that it is not possible to unambiguously identify specific macromolecules from the mass spectrometer data. Nevertheless, the large amounts of $H_2CO$ injected into the coma suggest that POM, or perhaps POM fragments such as small oligomers of formaldehyde, must be present in the coma (Boice et al., 1990).

Recent laboratory work on the thermal and photolytic degradation of POM has been performed by Cottin et al. (2001b). When their results were incorporated into a coma model, they were able to show that the $H_2CO$ production rate in comet Halley could be matched if $\sim 7\%$ of the mass of cometary grains is accounted for by POM (Cottin et al., 2001b). Using the model parameters of Cottin et al. (2001b) we have recently modelled the injection of deuterated formaldehyde into the coma (Rodgers and Charnley, 2002b). We find that, if the D/H ratio in the dust parent is different to that in formaldehyde ice in the nucleus, the $HDCO/H_2CO$ ratio in the coma will change with cometocentric distance. Hence, unlike species with only a direct source, the coma D/H ratios in species with extended sources cannot easily be used to derive D/H ratios in the nuclear ices. However, if POM forms via polymerization of $H_2CO$, one would expect equal D/H ratios in both sources of formaldehyde. HDCO and $D_2CO$ have both been detected in the interstellar medium, where they are often observed with enormous fractionations (e.g., Loinard et al., 2001), and the relative $H_2CO : HDCO : D_2CO$ ratios may be used to constrain the origin of the formaldehyde (Turner, 1990). Kuan et al. (2002) reported a tentative detection of HDCO in comet Hale–Bopp. These isotopes should therefore be searched for in future comets.

## 5.2. HNC AND HCN

Cometary HNC was first detected in Hyakutake, where it was observed with a HNC/HCN ratio of 6%. HNC has since been seen in five more comets, and it is now known to have an extended source in the coma. Detailed chemical modelling of potential HNC production mechanisms have demonstrated that ion-molecule chemistry cannot produce the observed amounts, but that reactions involving suprathermal H atoms may be effective in large, active comets such as Hale–Bopp (Rodgers and Charnley, 1998, 2001b). However, the detection of an extremely large HNC/HCN ratio of $\approx 30\%$ in comet Ikeya–Zhang appears to show that the source of HNC in all comets must be photolytic decomposition of some unknown organic refractory parent (Butner et al., private communication). Additional evidence for

a dust source of HNC comes from the observations of Blake et al. (1999) who mapped the HNC distribution in Hale–Bopp, and demonstrated that the HNC/HCN ratio peak was offset from the nucleus, in the direction of a dust jet.

Although HCN is clearly a parent species, maps of the HCN distribution in Hale–Bopp also show evidence for an additional extended source, accounting for ∼15% of the HCN at large cometocentric distances (Wright et al 1998; Veal et al., 2000). Maps of the HCN emission in Ikeya–Zhang show that the HCN peak was offset from the nucleus, again suggesting an additional coma source (Charnley et al., 2002; Butner et al., private communication). The parent of the CN radical in the coma is also an open question. Although some of the CN can be accounted for by photodissociation of HCN, it is not clear that all the CN can be produced this way (Festou, private communication). Indeed, the spectacular spiral images of CN in comet Halley (A'Hearn et al., 1986) suggest that CN production also has a strong connection with cometary dust. Hence, the same material that produces HNC in the coma is also a viable candidate for the extended sources of HCN and CN.

Although the refractory parent of HNC is currently unknown, laboratory measurements may help to constrain its identity. Hexamethylenetatramine (HMT, $C_6H_{12}N_4$) is known to form in significant amounts following UV photolysis or proton irradiation of interstellar ice analogs (Bernstein et al., 1995; Cottin et al., 2001a). Further photolysis of HMT is known to lead to nitriles, and the injection of such material into the coma was proposed by Bernstein et al. (1995) to account for the extended CN source in comets. Alternatively, Rettig et al. (1992) proposed that HCN polymerization may provide the energy source necessary to drive cometary outbursts, and speculated that these polymers may account for the CN source in comets. Clearly, more laboratory experiments on HCN polymerization and the photolytic yields of —CN— based polymers are required before we can determine the parent of HNC in comets.

## 6. The Nucleus

### 6.1. PHYSICAL PROPERTIES

A more detailed review of our current understanding of the physical nature of cometary nuclei is given by Rickman (presentation at IAU Coll. 186, Tenerife, 2002) and Prialnik (2002). Here, we concentrate on those aspects which control the nuclear outgassing, and so determine the relation between coma and nuclear chemical abundances. Key physical parameters are the visual albedo and infrared emissivity of the nucleus, which determine the fraction of the incident solar energy that is available to drive ice sublimation and thermal processing of the nuclear ices. Visual images of the nuclei of comets Halley and Borrelly show the surface to be dark, and a visual albedo of 0.04 is often assumed as a typical value (e.g., Jewitt, 1991). Based on these low visual albedoes, and on the properties of material

thought to be relevant to comet nuclei, an infrared emissivity of $\approx 0.9$ is usually assumed (Klinger, 1999).

Cruikshank et al. (1991) identified the spectroscopic signatures of CN-bearing molecules in the reflectance spectra of cometary dust, and proposed that the darkness of cometary surfaces could be explained if complex organic HCN polymers were mixed with the ice. More generally, the presence of any kind of large organic molecules in ices leads to a low reflectivity (Greenberg, 1986). A recent study by Jewitt (2002) has shown that the colours of cometary nuclei and Kuiper Belt objects are significantly different. Jewitt attributes this to the formation of a "rubble mantle" on the surface of the comet as it approaches the sun. This study demonstrates that the nature of the nuclear surface changes over time, and depends on the orbital history of the comet.

A number of laboratory studies of comet-like ice : dust mixtures have been performed, the largest of which was the series of KOSI experiments carried out at the German Space Agency (see e.g., Kochan et al., 1989; Sears et al., 1999). These experiments have demonstrated that the surface layers of comets can become rapidly depleted in ices, leading to the formation of a dust mantle. Hence, the outgassing is controlled by the sublimation of volatile ices from subsurface layers. The distance of the sublimation front from the surface depends on the volatility of the molecule, and so stratified layers develop with distinct chemical compositions (cf. Rickman, 1991). These experiments also provide information on the diffusivity of gas phase molecules through the porous structure, and on the thermal conductivity of comet-like materials. These data can then be used to calibrate numerical models of the heat and gas flow in cometary nuclei (Spohn and Benkhoff, 1990; Skorov et al., 1999; see Section 7 below).

## 6.2. CHEMICAL COMPOSITION

As discussed in Section 4, the molecular inventory of cometary ices is inferred from observations of the coma. However, models of the outgassing occurring at the nuclear surface (and interior) have demonstrated that the relationship between nuclear and coma abundances is not always straightforward (e.g., Huebner and Benkhoff, 1999). The rate at which volatiles are released depends not only on the abundance, but also on the enthalpy of sublimation, which in turn depends on the microscopic structure of the ices. Laboratory work on low-temperature $H_2O$ ices has shown that, depending on the temperature and the rate at which the ice is formed, a variety of different microscopic structures are possible. At low temperatures water forms a high density amorphous ice, which changes gradually to a low-density amorphous phase upon heating to 38–68 K (Jenniskens and Blake, 1994). The physical properties of the amorphous phases can be very different to those of the hexagonal $H_2O$ ice we are used to (e.g., Jenniskens et al., 1995). There is also laboratory evidence that a viscous liquid phase can coexist with the ice at temperatures between 140–210 K. This suggests that comets could episodically

contain a subsurface liquid layer (Jenniskens et al., 1997). There is no observational evidence for the existence of this hypothetical layer although Blake et al. (1999) have speculated that chemical reactions in this layer may alter the HNC/HCN and D/H ratios in the nuclear material as it outgasses.

The amorphous-crystalline transition occurs in the laboratory at ∼130 K (Prialnik and Bar-Nun, 1987). This process releases latent heat, and has been proposed as the energy source which drives cometary outbursts (Patashnik et al., 1974). 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. Models of the protosolar nebula have shown that an accretion shock develops, and material falling into the protosolar disk from the natal cloud may have undergone substantial heating (e.g., Chick and Cassen, 1997). Although the shock was undoubtedly effective in vaporizing material entering the inner solar nebula, it is currently uncertain as to whether material entering the outer regions of the nebula would also have been affected. If so, it is possible that the evaporated $H_2O$ eventually recondensed on the grains in crystalline form. Certainly, the chemical composition of the recondensed ices will be altered from the original interstellar state (Lunine et al., 1991).

The sublimation rates of interstellar and cometary ice analogs have been measured in the laboratory. To first order, the sublimation is controlled by a Boltzmann factor, $\exp\{-E_b/kT\}$ where $E_b$ is the surface binding energy, and so the sublimation rate is extremely sensitive to the temperature. Typical values for $E_b/k$ range from 960 K for pure CO ices up to 5770 K for amorphous $H_2O$ (Sandford and Allamandola, 1988, 1990, 1993; Fraser et al., 2001). These experiments also show that the binding energies for mixed ices can differ substantially from the pure substance. For example, CO frozen on a water ice substrate has a value of $E_b/k = 1740$ K, almost twice as large as that for pure CO (Sandford and Allamandola, 1990). Experimental work on the trapping and outgassing of minor species in water ice reveal a complex temperature dependence for the sublimation rate (e.g., Bar-Nun et al., 1985). Therefore, it is probably very naïve to assume that cometary ice sublimation occurs at the same rate as measured from experiments on the pure substance. Rather, the release of molecules from cometary ices will depend in a complex fashion on the overall chemical composition of the ice, and the microscopic structure of the icy matrix.

It is often assumed that minor volatiles are trapped in the water ice as clathrate-hydrates. However, the only observed cometary species which have been demonstrated to form clathrates in the laboratory are $CH_3OH$ and $H_2S$ (Notesco and Bar-Nun, 2000). Clathrate structures are closely packed $H_2O$ networks linked together by hydrogen bonds, which are able to encage small molecules. Encaged $CH_3OH$ molecules, e.g., lead to the formation of type II clathrates. Clathrate hydrates of type II have been unambiguously identified during the warm up of

$H_2O$—$CH_3OH$ mixtures when $H_2O$ was twice more abundant than $CH_3OH$ (Blake et al., 1991). The formation of segregated boundary layers which are associated with clathrate formation have been identified in laboratory experiments of interstellar ice analogs (Blake et al., 1991; Ehrenfreund et al., 1999). This provides evidence that clathrates can be already formed in interstellar icy particles and be later integrated into comets. However, most species are likely to be incorporated into amorphous water ice, and so will find it easier to escape from the $H_2O$ ice than if they were clathrated.

Experimental work on the differential trapping rates of $N_2$ and CO has shown that CO is trapped in amorphous water ice more efficiently than $N_2$ (Notesco and Bar-Nun, 1996). Hence, this may explain the nitrogen depletion in comets. Alternatively, Charnley and Rodgers (2002) proposed that the nitrogen deficit could be explained if ion-molecule chemistry eroded $N_2$ into atomic N which did not freeze out. This theory explains the origin of the large $^{15}N/^{14}N$ ratios seen in some meteorites and interplanetary dust particles (e.g., Messenger and Walker, 1997), and could be tested if the $^{15}NH_3/^{14}NH_3$ ratio could be measured in a comet.

For comets closer to the sun than $\sim 3$ AU the outgassing is dominated by water ice. However, the most volatile species may already be depleted, having already escaped at larger heliocentric distances. For example, when comet Hale–Bopp reached a heliocentric distance of 3 AU on its inward journey a dip in the CO production rate was observed (Biver et al., 1997). This behaviour is reproduced in models of the nuclear outgassing (e.g., Prialnik, 1999), and can be understood in terms of the transition from CO-driven sublimation (from deep within the nucleus) to a $H_2O$-controlled regime involving the water-rich but CO-poor surface layers.

## 7. Models of Nuclear Outgassing

A number of detailed models of nuclear outgassing have been developed (e.g., Prialnik, 1992; Espinasse et al., 1991; Tancredi et al., 1994; Orosei et al., 1995; Enzian et al., 1997; Benkhoff and Boice, 1996). Although the models differ in their details, the fundamental approach is similar. Essentially, the problem involves solving the set of coupled diffusion equations describing the evolution of the porous nuclear matrix; one for the heat flow, and one for each molecular species in the ices. The results of the various models were compared by Huebner et al. (1999), and although the agreement for the surface temperature and $H_2O$ production rate was reasonably good, predictions of the outgassing of minor volatiles such as CO were found to be very model dependent.

Generally, these models find that as a comet approaches the sun, a thermal heat wave penetrates beneath the surface of the nucleus, releasing volatile species from subsurface layers. These species then diffuse through the gaps in the porous nucleus, until they either reach the surface and escape, or they re-freeze in a deeper, colder layer of the nucleus. Thus, the surface layers become gradually depleted in

the most volatile species, and sublimation fronts develop at different depths for different species (Huebner and Benkhoff, 1999). The depth of the sublimation fronts depends crucially on the thermal conductivity of the nucleus, a parameter whose value is highly uncertain. The saturated vapour pressures control the outgassing rate. For water, CO and/or $CO_2$, values are calculated assuming a simple exponential temperature dependence, and generally use the values appropriate for the pure substance. Some models assume that the CO is trapped as a gas, and hence it does not sublimate as such, but is released when $H_2O$ crystallizes. As discussed in the previous section, many of these assumptions are suspect and the outgassing behaviour of real cometary ices is likely to be much more complex.

Laboratory studies provide important input for comet nucleus models (e.g., Sears et al., 1999) and experiments designed to understand recent ISO data on the composition of interstellar ices (e.g., Ehrenfreund et al., 1998) may also have important implications for pre-cometary ices and for models of the cometary nucleus. In particular, if $CO_2$–$CH_3OH$ intermolecular complexes (see Figure 1) are also present in comets, it may significantly affect the $CO_2$ and methanol production rates.

Thus, to quantitatively investigate the effects on the molecular outgassing rates of different ice phases and compositions, we have begun to develop a physico-chemical model of the nucleus (own work, unpublished). Here we outline the essential ingredients for comet nucleus models and present some preliminary, exemplary, calculations which serve to illustrate the need for a synergy between experiment and theory. A more extensive description of these models can be found in Prialnik (2002).

The heat diffusion equation can be written:

$$(\rho C)\frac{\partial T}{\partial t} = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\kappa\frac{\partial T}{\partial R}\right) + Q, \tag{1}$$

where $R$ is the radial distance, $(\rho C)$ is the heat capacity of the nuclear matrix and $\kappa$ is the thermal conductivity. $Q$ represents the net heat source due to all physical and chemical processes occurring in the nucleus, principally crystallization of water ice and sublimation of molecules. The diffusion equation for the partial pressure of the gas phase species $x$ in the pores is:

$$\frac{\partial P_x}{\partial t} = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2 D_x\frac{\partial P_x}{\partial R}\right) + S, \tag{2}$$

where $D_x$ is the diffusion coefficient for $x$, which in general will depend on $P_x$, $T$, and the pore size and molecular mass. $S$ is the source term due to sublimation of the ice. Equations (1) and (2) are coupled through the fact that sublimation causes a net loss of energy, whereas freeze out releases latent heat. In practice, Equation (2) is solved only in the outer layers of the nucleus, since the sublimation timescale is much shorter than any other relevant timescales (Tancredi et al., 1994).

TABLE I

Model parameters for Hale–Bopp nucleus

| Quantity | Value |
|---|---|
| Semimajor axis (AU) | 186.6 |
| Eccentricity | 0.9951 |
| Nuclear radius (km) | 20 |
| Porosity | 0.54 |
| Temperature (K) | 20 |
| Pore size (mm) | 1 |
| Visual albedo | 0.04 |
| Infrared emissivity | 0.9 |

TABLE II

Physical parameters for comet nucleus model

| Quantity | Dust | $H_2O$ (cryst) | $H_2O$ (amorph) | CO |
|---|---|---|---|---|
| $\rho_o$ (g cm$^{-3}$) | 0.336 | 0 | 0.336 | 0.034 |
| $\rho$ (g cm$^{-3}$) | 2.5 | 0.92 | 0.92 | 0.92 |
| $c$ (J kg$^{-1}$ K$^{-1}$) | 1300 | $7.5T + 90$ | $7.5T + 90$ | $7.5T + 90$ |
| $\kappa$ (W m$^{-1}$ K$^{-1}$) | 0.1 | $567/T$ | $7(-5)$ | $7 \times 10^{-5}$ |
| $h$ | 0.01 | 0.01 | 0.01 | 0.01 |
| $H$ (kJ mole$^{-1}$) | – | 51.07 | 51.07 | 6.35 |
| $P_{sat}$ (Pa) | – | $3.56(12)e^{-6142/T}$ | $3.56(12)e^{-6142/T}$ | $1.26(9)e^{-764/T}$ |
| $r$ (Å) | – | 3.5 | 3.5 | 3.5 |

$a(-b) = a \times 10^{-b}$.

Physical quantities listed are: Initial density ($\rho_0$), solid density ($\rho$), specific heat ($c$), heat conductivity ($\kappa$), Hertz factor ($h$), sublimation enthalpy ($H$), saturation vapour pressure ($P_{sat}$), and molecular diameter ($r$).

Therefore, following Orosei et al. (1995) we assume that wherever the ice of a particular molecule is present, the gas phase pressure of that molecule in the pores is equal to the saturation pressure at the appropriate temperature.

At its current stage of development the model considers only $H_2O$, CO, and a dust component. In the results shown below we assume that dust is removed from the cometary surface at the same rate as water ice, i.e., we neglect the build up of a dust mantle. In reality, the surface will become depleted in ice and the "active area" will decrease with time. However, the details of these changes will depend on the dust size distribution, and the threshold outgassing rate at which dust
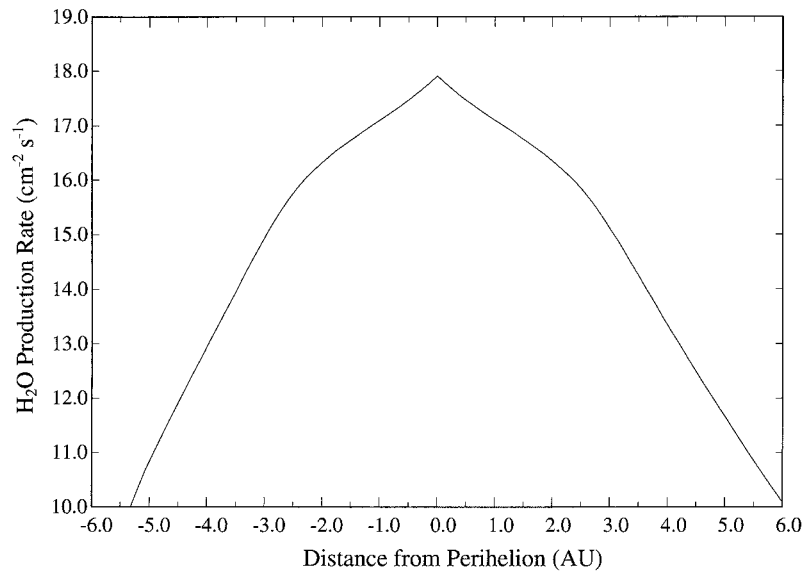
*Figure 4.* Molecular production rate of $H_2O$ (solid line) calculated for comet Hale–Bopp. See text for details.

particles of a certain size can be lifted from the surface. We assume a spherically symmetrical nucleus, and adopt the "fast Rotator" approximation, i.e., the nucleus is assumed to be illuminated isotropically. The "fast rotator" approximation and our assumption that the dust is also removed with the gas is unrealistic, however such simple models are necessary to benchmark the code against existing calculations (cf. Huebner et al., 1999). Hence, physical parameters for the nuclear constituents were taken from Huebner et al. (1999) and are summarised in Tables I and II. We followed Orosei et al. (1995) in calculating the $D_x$. Although much of the physics has been crafted from existing models, an important difference is that we have used a powerful implicit algorithm capable of efficiently solving large systems of highly nonlinear diffusion equations (Charnley, 1988). This approach will ultimately be useful in treating multidimensional problems (e.g., Enzian et al., 1997) and those involving non-isotropic diffusion parameters.

Figure 4 shows the evolution of the molecular production rates in a demonstrative model run using parameters appropriate for Hale–Bopp. The predicted water outgassing rate is in reasonable agreement with the measured values.

Figure 5 shows the temperature profile inside the nuclear surface, at three times pre-perihelion and three times post-perihelion. The heat wave which penetrates the nucleus is a diffusion wave, and so the depth is roughly proportional to $t^{0.5}$. The steep, well defined edges of the curves are caused by the crystallization of the water ice; once the temperature reaches a certain critical value the ice anneals, releasing latent heat. Due to its regular structure, crystalline ice has a much higher thermal conductivity than amorphous ice, and so once the ice has annealed it remains in
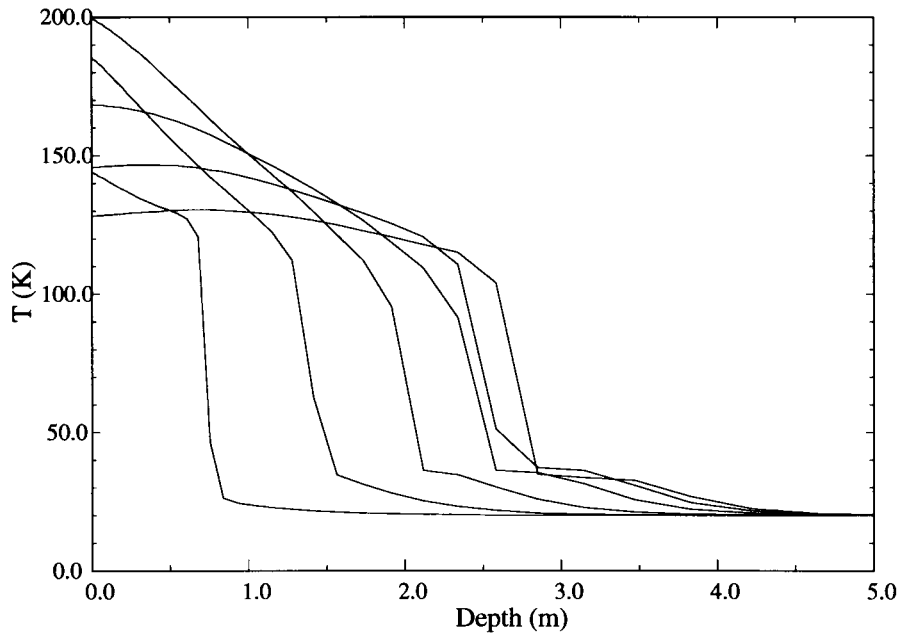
*Figure 5.* Temperature profiles within the nucleus. Lines are drawn for six different times – 0.75, 1.5, 2.25, 3.0, 3.5, and 4.1 years. Later times correspond to deeper penetration of the thermal wave.

good thermal contact with the outer layers. Note that, after four years of evolution, the depth of the thermally processed layer is only $\sim$ 3 m. For comparison, Tancredi et al. (1994) find much deeper penetration of the heat wave, over 100 m. However, this is due to the much larger thermal conductivity assumed in their model, since the depth varies as $\kappa^{0.5}$. This shows the importance of understanding the physical properties of the nucleus, many of which are not well constrained.

Currently, there remain many uncertainties regarding the appropriate parameters to use in such models. For example, the surface temperature of the comet depends very sensitively on the ice coverage of the surface. Dusty ice-free surfaces are much hotter than icy surfaces, but the overall molecular production rates are lower, since most of the absorbed solar energy is immediately reradiated. The $H_2O$ production rates of most comets can only be reproduced if one assumes an "active" surface, i.e., that water ice is present on the surface. However, the recent encounter of Deep Space 1 with comet Borrelly demonstrated that this comet had a very hot surface, consistent with no ice being present (Soderblom et al., 2002b).

Despite the many uncertainties involved in such models, we may still hope to use them to understand the structure of cometary ices. This is because, fundamentally, the outgassing of particular species depends on the surface binding energy via a Boltzmann factor. Hence, the sublimation rate is almost a step-function in temperature, and significant outgassing is only possible once a certain critical temperature is reached. Thus, by comparing gas production rates vs. heliocentric distance, we

can determine the relative volatilities of different species. Comparison with models will help establish if these species must be present as pure substances, clathrates, or impurities in amorphous water ice.

## 8.  Conclusions

The simplest prescription for deriving nuclear composition from coma observations assumes that the molecules come directly from the nucleus, and any chemical processing in the coma other than photochemistry can be neglected. This prescription has been invalidated for several species (CO, $H_2CO$, HNC; see Section 4). Models of the coma have demonstrated that these molecules may be injected following the thermal or photolytic decomposition of refractory organic material. Models of the nuclear outgassing also demonstrate that there is no simple correlation between nuclear and coma abundances. In the future cometary observations may have to be interpreted in the context of a nucleus whose ices are stratified in density, temperature and porosity.

Laboratory data allow us to identify partly the dust and ice components in the interstellar medium and help us to constrain the composition of cometary nuclei as well as their common link. Crystalline water ice, which probably makes up a large fraction of a comet, was detected by the ISO in the coma of Hale–Bopp at 2.9 AU from the sun through its emission features at 44 and 65 $\mu$m (Lellouch et al., 1998). Analyses of the 3 $\mu$m band profile in VLT spectra of interstellar clouds indicate that the water ice is mainly amorphous, but can be also partly crystallized in dense clouds. Water ice, formed at low temperatures in the interstellar medium is believed to be in the high-density amorphous form, an ice structure without open cages. If this is the predominant material comets are made of, the transformation into the low-density amorphous ice upon heating will cause stress due to expansion. This will form cracks in the cometary nucleus, which subsequently could result in active vents or in the worst case to fractionation of the nucleus (Jenniskens and Blake, 1996). The structure of the nuclear ice component which may have coexisting amorphous/crystalline phases and clathrates will also strongly influence the cometary outgassing properties.

In general the outgassing of cometary volatiles is related to the solid phase of the interstellar medium. As for the ISM water is the dominant sublimating component, followed by CO and $CO_2$. It is important to state that neither ethane, nor acetylene or HCN (molecules which are observed in comets) have been identified in the ice phase of interstellar grains (Boudin et al., 1998; Ehrenfreund and Charnley, 2000). Furthermore no S-bearing species, except OCS in very small abundances, is observed in the ice. This is in contrast to cometary observations. The abundances we use for comparing interstellar and cometary data are mostly derived from the observations of high-mass protostars. Low mass protostars evolve more slowly and show partly a different ice composition (e.g., for CO, $CO_2$, $CH_3OH$). The sensitiv-

ity of large telescopes allows us to observe these faint objects in telluric accessible windows. Observations of low-mass stars will provide important constraints for the icy material which was originally available for incorporation into solar system material. Strong progress on the characterization of macromolecular carbon in comets is expected from the use of new sensitive techniques for the analyses of cosmic dust analogs and meteoritic material.

Future space missions, such as ROSETTA, which will land on a comet and study directly the nuclear composition, will improve significantly our knowledge on the origin and structure of comets.

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