

# Observations of molecules in comets

D. Despois<sup>1</sup>, N. Biver<sup>2</sup>, D. Bockelée-Morvan<sup>2</sup>, J. Crovisier<sup>2</sup>

<sup>1</sup>Obs. de Bordeaux, OASU/L3AB, BP89, F-33270 Floirac, France

<sup>2</sup>LESIA, Obs. de Paris, 5 pl. Janssen, F-92195 Meudon, France  
email: despois@obs.u-bordeaux1.fr

**Abstract.** Comets are among the most primitive bodies of the Solar System, and their chemical composition is rich in information on the protosolar nebula and its possible connection with interstellar cloud chemistry. Comets are also a source of light atoms and probably of prebiotic organic molecules for the early Earth.

We know better and better cometary volatiles through spectroscopy, mainly at infrared and radio wavelengths. Another crucial component of cometary matter — organic refractories — is however still poorly characterized.

We summarize here the  $\sim 30$  abundances and  $\sim 20$  upper limits obtained on cometary volatiles and highlight a few species and problems: ethylene glycol, NS, HNC/HCN,  $^{14}\text{N}/^{15}\text{N}$ , CN origin,  $\text{CS}_2$ , PAHs, and  $\text{H}_2\text{O}$  measurements. Comet-to-comet variations and comet internal heliocentric variations can now be studied, and cometary comas are mapped with a variety of techniques. We list temperature indicators: they can help understand the relation between IS and cometary matters, which present both a global similarity, and marked differences, like the high ethylene glycol content of comets.

We conclude by picking up a few key problems to be addressed by future ground-based and space instruments or by cometary sample analysis. For many species, however, laboratory data are missing on spectroscopy, photodissociation and collisions with  $\text{H}_2\text{O}$ .

**Keywords.** Comet: general, astrochemistry, Solar System: formation, planetary systems: protoplanetary disks

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## 1. Introduction

On 4th of July, 2005, comets were again a hot topic, as the Deep Impact projectile hit the  $5\times 7$  km nucleus of comet 9P/Tempel 1. The experiment has brought a wealth of information on the physics of the nucleus, surface details and strength of cometary matter (A'Hearn et al. 2005); it may also have provided new insights in the chemical composition: beside known species, Spitzer IR observations (Lisse et al. 2005) may have detected  $\text{Al}_2\text{O}_3$ , and PAHs (already tentatively detected in 1P/Halley, see below). More results are given in Meech et al. (2005) and Keller et al. (2005).

Comets are the most pristine bodies in the Solar System. Their astrochemical interest is at least fourfold: i) they hold a wealth of information on physics and chemistry in the protosolar nebula (PSN) ii) they offer a link, at least partial, to the chemistry of the parent cloud from which the Solar System has formed iii) they are, through violent impacts as well as through smooth delivery of dust particles (meteors, micrometeorites, IDPs) one source of carbon and prebiotic molecules for the early Earth; iv) finally, as all astronomical objects presented in this Symposium, they are a remarkable laboratory for molecular physics and chemistry. Kinetic temperature in the coma first decreases from  $\sim 200$  K (water ice sublimation) to a few 10 K or even less, due to adiabatic expansion, then warms up again due to heating by photodissociation. Rotational populations, first at LTE, progressively decouple from gas translational energy, due to rapid decrease in density and collisions far from the nucleus; solar radiation then takes over as the main source

of excitation. For vibrational and electronic states, even very close to the nucleus solar excitation dominates, provided the coma is not optically thick. Coma density can be as high as  $10^{12} \text{ cm}^{-3}$  close to the nucleus surface, and decreases rapidly to the interplanetary level ( $\sim 1 \text{ cm}^{-3}$ ). Gas expansion velocities are on the order of 1 km/s. The dominant coma species is usually water, except far ( $> 4 \text{ AU}$ ) from the Sun, where CO overtakes this role. Ions and radicals are photoproduced which means that ion-molecule and radical reactions are possible; ions finally interact with the solar wind, building up the plasma tail.

Time scales for chemistry are very diverse. The formation of icy planetesimals can be as short as  $2.5 \cdot 10^5 \text{ yr}$  according to models, and has to take place when a gaseous disk is still around the Sun, ie during the first  $\sim 10 \text{ Myr}$  of the Solar System—note that some ingredients, especially among dust particles, are prestellar, thus older. The formation is followed by a 4.5 Gyr mostly dormant phase, in one of the two comet reservoirs: the Oort Cloud or the Kuiper Belt. Despite the generally very low temperature ( $< 30 \text{ K}$  ?) of the comet nucleus, it is not certain that such a long period is devoid of any chemical transformation (an episode of liquid water is even considered as possible in the core of the largest (a few 100 km) KB objects). The active phase during which the coma is observed typically lasts months, whereas the lifetimes of sublimated molecules range from  $10^3$  to  $10^6 \text{ s}$  (at 1 AU).

For physicists and chemists unfamiliar with comet science, a general introduction is given in Despois and Cottin (2005), and Crovisier (2004), with special emphasis on the connection to Astrobiology. A very recent, deep and complete summary on cometary science is the book *Comets II* (Festou et al. eds, 2004), where the chapters by Bockelée-Morvan et al. (parent species) and Feldman et al. (secondary species) are the most directly relevant to Astrochemistry. The possible connection between ISM and comets is addressed in detail by Irvine et al. (2000) and Ehrenfreund et al. (2004). We will discuss in the following mainly cometary volatiles; when there is no reference to other authors, the original data are from Bockelée-Morvan et al. (2000) and Crovisier et al. (2004a,b) (detections and upper limits in comet Hale-Bopp), and Biver et al. (2002a, 2005a), Crovisier et al. (2005) (inter and intra comet variations).

## 2. Cometary volatiles composition

Comets, if coma composition reflects nucleus composition, are made of roughly equal masses of dust and ices (within a factor of 10, depending on the comet). Dust itself is half rocky material (eg silicates), half organic refractories ("CHON" particles). We will mainly discuss here the volatile composition. One should however keep in mind that: i) many complex molecules may be hidden in the organic refractories, and are not yet accessible to precise identification; ii) macromolecular carbon (e.g. heterogeneous copolymers, cf Fomenkova 1999) may be the dominant form of carbon in these refractories as it is in meteorites (Binet et al. 2004).

Table 1 gives "typical" cometary volatiles abundances, together with the range observed in various comets, and the number of comets observed/detected in a given species. "Typical abundances" means in practice in most cases coma abundances from C/1995 O1 (Hale-Bopp) observed near  $r_h = 1 \text{ AU}$ ; however, a few species have been measured under more favourable circumstances ( $\text{CO}_2$ ) or only ( $\text{S}_2$ ,  $\text{C}_4\text{H}_2$ ) in other comets. The comet-to-comet dispersion, comet internal variation, and coma vs nucleus abundance discussions (including differential sublimation and coma chemistry) should not be forgotten when using these data.

It is of prime importance, when comparing these abundances to laboratory experiments on interstellar / cometary ice analogs, or to chemical models of ISM or protosolar

Cometary Volatiles	category	Molecule	Hale-Bopp Abundance (H2O= 100)	Intercomet variation	comets detected +upperlimits (a)	Notes	
H		H2O	100				water
		H2O2	<0.03				hydrogen peroxide
C,O		CO	23	<1.4-23	9+8	variable, extended source	carbon monoxide
		CO2	6	2.5-12	4	IR, UV from various comets	carbon dioxide
C,H		CH4	1.5	0.14-1.5	8	IR	methane
		C2H6	0.6	0.1-0.7	8	IR	ethane
		C2H2	0.2	<0.1-0.5	5	IR	acetylene
		C4H2	0.05?			IR From Ikeya-Zhang <prelim.val.)< td=""> <td>diacetylene</td> </prelim.val.)<>	diacetylene
		CH3C2H	<0.045				propyne
C,O,H		CH3OH	2.4	<0.9-6.2	25+2		methanol
		H2CO	1.1	0.13-1.3	18+3	extended source	formaldehyde
		CH2OHCH2OH	0.25				ethylene glycol
		HCOOH	0.09	<0.05-0.09	3+2		formic acid
		HCOOCH3	0.08				methyl formate
		CH3CHO	0.025				acetaldehyde
C,O,H upper limits		H2CCO	<0.032				ketene
		c-C2H4O	<0.20				oxirane
		C2H5OH	<0.1			trans	ethanol
		CH2OHCHO	<0.04				glycolaldehyde
		CH3OCH3	<0.45				dimethyl ether
		CH3COOH	<0.06				acetic acid
N		NH3	0.7	<0.2-1	4		ammonia
		HCN	0.25	0.08-0.25	32+0		hydrogen cyanide
		HNCO	0.1	0.02-0.1	4+2		isocyanic acid
		HNC	0.04	<0.003-0.035	12+3	Variable with rh	hydrogen isocyanide
		CH3CN	0.02	0.013-0.035	9+2		methyl cyanide
		HC3N	0.02	<0.003-0.03	3+7		cianoacetylene
		NH2CHO	0.015				formamide
N upper limits		NH2OH	<0.25				hydroxylamine
		HCNO	<0.0016				fulminic acid
		CH2NH	<0.032				methanimine
		NH2CN	<0.004				cyanamide
		N2O	<0.23				nitrous oxide
		NH2-CH2-COOH	<0.15			conformer I	glycine I
		C2H5CN	<0.01				cianoethane
		HC5N	<0.003				cyanobutadiyne
S		H2S	1.5	0.13-1.5	15+5		hydrogen sulfide
		OCS	0.4	<0.09-0.4	2+5	Extended source	carbonyl sulfide
		SO	0.3	<0.05-0.3	4+1	Extended source	sulfur monoxide
		SO2	0.2				sulfur dioxide
		CS2	0.17	0.05-0.17	15+3	from CS	carbon disulfide
		H2CS	0.02				thioformaldehyde
		S2	0.005	0.001-0.25	5	UV; from Hyakutake	disulfur
		CH3SH	<0.05				methanethiol
		NS	0.02	<0.02-0.02	1+1	Parent molecule ??	
P		PH3	<0.16				phosphine
Metals		NaOH	<0.0003				sodium hydroxide
		NaCl	<0.0008				sodium chloride

disk / nebula, to take into account both detections and upper limits. One should however keep in mind that the modelling used to derive upper limits is less elaborate than that used for the major species, e.g. H<sub>2</sub>O or HCN: LTE is assumed, and photodissociation rates are in several cases only educated guesses — by lack of precise laboratory data. However, radio single dish observations of comet Hale-Bopp by Crovisier et al 2004a did not suffer too much of these approximations, as the inner coma inside the beam was dense and little affected by photodissociation.

### 3. A few highlights

#### 3.1. Ethylene Glycol CH<sub>2</sub>OHCH<sub>2</sub>OH

Ethylene glycol (EG) has been securely identified in comet Hale-Bopp from IRAM 30m, PdBI and CSO observations (Crovisier et al. 2004b). 10 transitions with S/N 3 to 10, spanning the range 20 to 100 K in upper level energy were detected. The derived abundance is 0.29 % if one takes the rotational temperature of 77 K derived from the rotational plot, or 0.17 % if one adopts the 110 K average rotational temperature derived from other coma species. The photodissociation rate had to be assumed to a value  $2.10^{-5} \text{ s}^{-1}$  at AU, as no data were available; but the small size of the beam for these observations makes that this uncertainty is not too critical.

Ethylene glycol is a known IS species, observed for the first time by Hollis et al. (2002 and this Symposium) in Sgr B2. But some differences are striking when comparisons are made with other molecules. EG/CH<sub>3</sub>OH  $\sim$  0.1 in comets, whereas it is  $\sim$  0.001 towards Sgr B2; glycolaldehyde, CH<sub>2</sub>OHCHO, a molecule very similar to ethylene glycol, has not been detected yet in comets ( $x < 0.16$  EG) whereas it has comparable abundances in Sgr B2. And, more remarkably, ethanol, a simple alcohol (CH<sub>3</sub>CH<sub>2</sub>OH) has not yet been detected, when ethylene glycol, a dialcohol, has: CH<sub>3</sub>CH<sub>2</sub>OH/EG  $<$  0.4. All this seems to indicate a specific production mechanism in comets. Considering the high relative abundance of methanol in comets (2.5 % in Hale-Bopp, up to 6.2 % in other comets) it is tempting to invoke a direct formation from methanol, eg by ice irradiation. This has been experimentally performed with success (eg Moore, this Symposium, on H<sub>2</sub>O–CO<sub>2</sub> and H<sub>2</sub>O–CH<sub>3</sub>OH ices). One should note however that HCOOH is also produced in large quantities in these experiments, whereas it is even less abundant in comets ( $\sim$  0.3 EG) than in Sgr B2 ( $\sim$  EG).

#### 3.2. NS

The NS radical has been detected in comet Hale-Bopp by Irvine et al. (2000) with the JCMT through its  $J=15/2-13/2$   $a$  and  $f$  transition, with an abundance  $x_{\text{NS}} > 0.02$  %. NS is a well known IS molecule present in both warm and cold clouds. Searches through the  $J=11/2-9/2$   $e$  and  $f$  transition at 253 GHz in comet Hale-Bopp (Crovisier et al. 2004a) and 153P/Ikeya-Zhang (Biver et al. 2005a) led to upper limits of 0.01% and 0.02% respectively, assuming (?) a parent molecule distribution.

The origin of NS is not yet known. Could it be present as such in the ice? If it is a photodissociation product, which is the parent molecule? NH<sub>4</sub>SH (predicted as a cometary species by Fegley et al. 1993) is a possibility but its photodissociation is unknown. NH<sub>2</sub>SH is another candidate. No map exists, so we have no constraint on the lifetime of NS parent, which also prevents a good estimation of its production rate. The  $x_{\text{NS}} > 0.02$  % abundance in comet Hale-Bopp is a lower limit and assumes a NS photodissociation rate  $\beta \sim 0.1-2 \cdot 10^{-4} \text{ s}^{-1}$ . A chemical model has been proposed to produce NS by coma reactions, but it cannot account quantitatively for the NS abundance (Canaves et al. 2002).

### 3.3. HNC vs HCN

The HNC/HCN ratio is seen to decrease in the coma with increasing heliocentric distance  $r_h$ . Irvine et al. (1998) proposed a chemical conversion in the inner coma by ion-molecule reaction and electronic recombination of the molecular ion  $\text{HCNH}^+$  as in cold dark clouds. Reactions of HCN with rapid, suprathermal hydrogen atoms issued from photodissociation were shown to be more efficient, and capable to quantitatively explain comet Hale-Bopp results, but still not the presence of HNC in less dense comas (Rodgers and Charnley 2001, Charnley et al. 2002). To match the HNC/HCN vs  $r_h$  data (Biver et al 2002b, 2005a; Irvine et al. 2003), thermo-desorption from grains is also proposed. Comet Hale-Bopp interferometric observations (Bockelée-Morvan et al. 2005a,b) and new observations (Biver et al 2005a, Crovisier et al. 2005), which show a plateau in HNC/HCN around 0.2 for  $r_h$  0.1–0.5 AU, favour thermo-desorption and do not seem to be compatible with HNC production by chemical reaction of a daughter species (H). Finally, it is not yet excluded that HNC could be stable in ice at very low temperature; but observations limit the HNC fraction from the nucleus to 6 % of HCN.

### 3.4. $^{15}\text{N}$ problem and the origin of CN

A  $^{14}\text{N}/^{15}\text{N}$  isotopic ratio of 140 ( $\pm 30$ ) in the CN radical has been systematically derived (Arpigny et al. 2003, Manfroid et al. 2005) from visible observations of Hale-Bopp and other comets, including Deep Impact target 9P/Tempel 1 (Meech et al. 2005); this is twice less than the solar value (270). This contrasts with the  $^{14}\text{N}/^{15}\text{N}$  ratio in HCN from radio observations ( $323\pm 46$  Jewitt et al. 1997,  $330\pm 98$  Ziurys et al. 1997), and with other isotopic abundances in cometary volatiles which are, within the (still large) error bars, close to solar :  $^{13}\text{C}$ ,  $^{18}\text{O}$ ,  $^{34}\text{S}$  (see eg Table 3 of Bockelée-Morvan et al. 2004, and Altwegg and Bockelée-Morvan 2003). In comet Halley, strongly non-solar  $^{12}\text{C}/^{13}\text{C}$  values had been found in a limited number of grains, indicating their presolar nature; however, on the average, isotopic ratios in the grains appeared to be solar; the low  $^{12}\text{C}/^{13}\text{C}$  ratio in HCN measured in comet C/1996 B2 (Hyakutake) by Lis et al (1997) is likely due to contamination by another line.  $\text{C}^{14}\text{N}/\text{C}^{15}\text{N}$  is up to now the only clearly non-solar isotopic ratio derived on the scale of the whole comet and involving heavy atom isotopes.

That HCN is not the unique parent of CN has also been questioned on other grounds: comparing HCN and CN parent scalelengths, HCN and CN production rates, or CN jet morphology (eg Fray et al 2005). This has lead to consider other parents:  $\text{HC}_3\text{N}$ ,  $\text{C}_2\text{N}_2$  or refractory nitrogenated compounds (Fray et al 2004). But the production of some CN from  $^{15}\text{N}$  rich grains does not suffice to reconcile  $^{14}\text{N}/^{15}\text{N}$  measurement in CN with the HCN data; there is currently no proposed explanation which works.

### 3.5. Detection of carbon disulfide $\text{CS}_2$

Since the detection of the daughter species CS in comet C/1975 V1 West (Smith et al. 1980), its parent has been sought, and various candidate parent molecules have been proposed, and discussed on photodissociation lifetime arguments. That of  $\text{CS}_2$ , proposed as CS parent as early as 1982 by Jackson et al., has been revised in the laboratory from 100 to 500 s (at 1 AU), whereas cometary data required about 1000 s (Feldman et al. 1999). The establishment of  $\text{S}+\text{CO}$  as main photodissociation path for OCS (Huebner et al. 1992) ruled it out as a candidate. This exemplifies the crucial role played by laboratory data in the interpretation of cometary observations.  $\text{CS}_2$  seems now to have been identified with confidence in 122P/de Vico, through 28 visible lines (Jackson et al. 2004). Laboratory experiments (supersonic molecular beam) are in progress to confirm that the line intensities are correct.  $\text{CS}_2$  would be the third parent molecule (with CO and  $\text{S}_2$ ) identified directly from UV/visible spectra.

### 3.6. *Polycyclic Aromatic Hydrocarbons (PAHs)*

The detection of PAHs, a major component of IS matter, would be an important relation between ISM and comets. The 3.28  $\mu\text{m}$  band of PAHs was seen in some comets, but not in Hale-Bopp, perhaps due to the large heliocentric distance (2.7 AU) where it was searched. This band is subject to blending with OH prompt emission and  $\text{CH}_4$  fluorescence emission. In comet Halley, a recent reanalysis of TKS data (Clairemidi et al 2004) added a tentative detection of pyrene  $\text{C}_{16}\text{H}_{10}$  to that of phenanthrene  $\text{C}_{14}\text{H}_{10}$  (Moreels et al 1993). PAHs are seen in laser ablation of those IDPs thought to be cometary in origin (Clemett et al. 1993). Recently PAH features have been seen in the IR spectrum of 9P/Tempel 1 after the impact of Deep Impact (Lisse et al. 2005). According to Kress et al. (2004), PAHs are not likely to be produced by the impact itself, as their formation, thermodynamically allowed, is not favoured kinetically. The search for PAHs in the cometary dust sample collected by Stardust will be extremely interesting (if they have survived the collection process).

### 3.7. *The $\text{H}_2\text{O}$ reference*

A new development which improves the measurement of relative abundances is the direct determination of  $\text{H}_2\text{O}$  production through space submillimetre observations. This complements the widely used but indirect technique using OH maser emission (Crovisier et al. 2002), ground based IR observations of hot bands of water (Dello Russo et al. 2004), narrow band UV OH emission (A'Hearn et al. 1995) and other techniques based on water photodissociation products (Feldman et al. 2004). SWAS (Bensch et al. 2004) and Odin (Lecacheux et al. 2003) have observed the  $1_{10}\text{--}1_{01}$  submillimetre line of water various comets. The  $\text{O}^{18}/\text{O}^{16}$  ratio could even be determined with precision with Odin in comet 153P/ Ikeya-Zhang (Lecacheux et al 2003). SWAS (Bensch, this Symposium), Odin (Biver et al. 2005b), and the smaller radio telescope MIRO on board Rosetta all attempted to follow 9P/Tempel 1 evolution after Deep Impact. Remarkable features are the pre-impact natural variability, and the line profile changes seen in Odin spectra during and a few hours after impact.

## 4. Comet variation and comet population homogeneity

### 4.1. *Comet-to-comet variation*

As a “first approximation”, for the sake of simplicity, and by lack of more complete data, comet composition has first been thought as universal. Dust-to-gas ratio variations were however already obvious (Rolfe and Battrick 1987) and CN has been used early (A'Hearn et al. 1995) to distinguish comet classes. We are now, due to the increased sensitivity in radio and IR instruments, at the beginning of a statistical investigation of the comet population based on volatiles. Biver et al. (2002a,2005a) and Crovisier et al. 2005 have now gathered data on a handful of comets, and dispersions in the abundances are given in Table 1. They remain generally within a factor 3 of the mean, except for the very volatile CO molecule. No clear correlation has yet been found with dynamical parameters characterizing the orbit.

### 4.2. *Comet internal heliocentric variation*

The study of heliocentric variation of cometary abundances is an important tool to discuss processes responsible for the production of parent molecules (Biver et al. 2002b, “Christmas tree plot”). Similar evolution is expected in a group of molecules if the release of a same major species ( $\text{H}_2\text{O}$ , or CO) controls their outgassing; any departure from

the average behaviour indicates on the contrary the interplay of other processes. Several have been proposed : chemistry in the coma (HNC vs HCN, cf above), differential sublimation (CO vs H<sub>2</sub>O) and release from grains (H<sub>2</sub>CO, and possibly CN). Less pronounced departures seem to affect even the production rate ratio of quite similar species like H<sub>2</sub>O and CH<sub>3</sub>OH (Biver et al 2002b., 2005a), and a layered nucleus model has been proposed to explain it (Rodgers and Charnley, this Symposium).

#### 4.3. Coma maps

Another important recent development is the ability to map at radio wavelength molecules in the coma. This allows us to address the origin (nuclear or not) and the photodissociation lifetime of a species, and to reveal structures ("jets") in the coma. Large scale maps (a few arcminutes, or a few 10<sup>5</sup> km) have been produced first point by point (Biver et al. 1999, Hirota et al. 1999) but more homogeneous maps are produced by detector arrays (QUARRY at FCRAO, Lovell et al. 1999) or raster techniques (NRAO 12m, Milam et al. this Symposium). High resolution interferometric maps (~ a few arcsecs or thousands of km) have been obtained on the very bright comet Hale-Bopp (Blake et al. 1999 at OVRO, Veal et al. 2000 at BIMA, Henry et al. 2002 at PdBI). A specific technique has been developed to analyse PdBI observation of Hale Bopp—model fitting in the *uv* plane—which allows us to reconstruct the main CO jet (Henry 2003, Bockelée-Morvan et al 2005a). Interferometric studies of comets are especially complex due to the time variability of the object, which limits the use of supersynthesis. In this respect ALMA, with its large instantaneous *uv* coverage, will bring a noticeable improvement.

#### 4.4. Temperature history and origin of cometary matter, connection to ISM

Comets are the most pristine bodies of the Solar System, but just how pristine are they ? How much information on the IS matter can we get from comets ? Several indicators exist which should inform us on the past temperature of cometary nuclei. In a simple evolution model of cometary matter formation, they could give us a "formation temperature" of cometary matter, dating back to the protosolar nebula. However, radial mixing in the PSN (eg Bockelée-Morvan et al. 2002), as well as vertical mixing between mid plane and high-*z* levels of the protostellar disk (cf disk structures presented in this Symposium) may have led to a complex history, possibly different for refractories and volatiles.

Important temperature indicators are :

- The presence/absence of volatiles and supervolatiles. The observation of CO at large heliocentric distances in comet Hale-Bopp (Biver et al. 2002b) may indicate that cometary matter incorporated it at low temperature (22 K for pure CO ice, up to several tens of K for CO-H<sub>2</sub>O mixture—the exact limit is still debated, and depends on the structure of the ice: amorphous, crystalline, clathrate). It may indicate that the nucleus internal temperature remained at such low temperatures for 4.5 Gyr. It may also be a constraint for models of the comet accretion process: perhaps CO was incorporated after the build-up of the ice-dust planetesimal, as the energy produced by the accretion process itself might have released this very volatile species.

H is strongly depleted in comets (FUSE observations of H<sub>2</sub> in the coma are an indication of coma production by H<sub>2</sub>O photodissociation). Rare gases, also very volatile, are crucial probes of the temperature history, but have not yet been convincingly detected (Bockelée-Morvan et al. 2004) An interesting case is N<sub>2</sub>. Its detection in comets through N<sub>2</sub><sup>+</sup> is ambiguous. Nitrogen as an element is depleted in comets (cf refs in Iro et al. 2003), a fact explained generally by the volatility of N<sub>2</sub>. However, some estimations give a very similar volatility for CO and N<sub>2</sub>, even on H<sub>2</sub>O ices, which is clearly a problem; clathrates have been proposed as a solution to this puzzle (Iro et al. 2003).

- Ortho/Para (O/P) ratios . They have been summarized by Kawakita et al. (2004). A recent development has been the use of a daughter species,  $\text{NH}_2$ , whose study can be used to trace the ratios in  $\text{NH}_3$ . The O/P ratios generally point toward a temperature of about 30 K, except in one case (comet C/1986 P1(Wilson)). No difference is yet seen between the various comets despite their different dynamical histories. But the meaning of this spin temperature is unclear: formation temperature of the molecule in the gas phase? formation on grain surface? equilibration with the comet interior during the 4.5 Gyr of its existence?

- Further constraints come from the isotopic ratios ( $\text{HCN}/\text{DCN}$  and  $\text{H}_2\text{O}/\text{HDO}$ , Mousis et al. 2000), the conservation of prestellar grains and from the crystalline and/or amorphous nature of silicates and water ice (still unknown).

While an overall correspondence exists between cometary and interstellar molecules found in hot cores (Bockelée-Morvan et al. 2000), definite differences exist, one of the most interesting being the suspected relatively high abundance of ethylene glycol in cometary ices. Another result still to be understood is the deuteration level ( $\text{HCN}/\text{DCN} \sim 2.3 \cdot 10^{-3}$  and  $(\text{D}/\text{H})_{\text{H}_2\text{O}} \sim 3 \cdot 10^{-4}$ ), and the presence of crystalline silicates (Crovisier et al. 1998; Hanner and Bradley 2004) not observed in the ISM (but observed around a Herbig AeBe star, Malfait et al. 1998).

## 5. Conclusion: What is important for the future

About 30 abundances of parent species, and nearly 20 upper limits on related compounds have already been determined in at least one comet. In parallel with the increase of this list, the following questions need to be addressed with high priority in the future: i) the homogeneity of the cometary nucleus; ii) the homogeneity of the comet population; iii) the nature of the organic refractories (which hide probably many complex molecules together with heterogeneous organic polymers). The resolution of all these issues would help to elucidate the origin of cometary matter, and to determine the respective roles of the interstellar matter (from the Solar System parent cloud) and of processing in the Protosolar Nebula. In view of the complexity of hot cores like Orion, of the processes in the protosolar nebula, and of the possible additional complexity of cometary chemistry, the correlation previously found between interstellar and cometary abundances remains a surprising observational fact, which needs to be explained.

Chemical analysis in situ (with Rosetta) and on samples (dust samples, with Stardust, and — hopefully soon — ice samples with a future space mission) may enlarge considerably (up to 100 species ?) the chemical inventory of comets. It will also provide the mean of chiral analysis, impossible to do from remote observing; this in turn will feed models of the early Earth for which comets may have been a source of prebiotic compounds. Ground-based and space-based teledetection (eg D/H ratio with Herschel/HIFI) will allow the statistical characterisation of the comet population(s). With high spatial resolution (large radio interferometers like ALMA and large optical telescopes, close-up maps from the Rosetta orbiter with eg MIRO or VIRTIS), we will study the comet variability and heterogeneity (analysing the respective chemical composition of jets vs more isotropic outgassing). Space observations will also provide the fundamental reference,  $Q_{\text{H}_2\text{O}}$ , as they have already begun to do.

The increased precision required to model comets asks for plenty of new laboratory measurements: spectroscopy (only a few unidentified lines at mm wavelength but more than 4000 in the UV/visible), photodissociation rates (most of them are now only educated guesses), and collision cross-sections with  $\text{H}_2\text{O}$ .

## References

- A'Hearn, M. F., Millis, R. L., Schleicher, D. G., Osip, D. J., & Birch, P. V. 1995, *Icarus*, 118, 223
- A'Hearn, M.F., Belton, M.J.S., Delamere, W.A. et al. 2005, *Science* 2005 0: 1118923
- Altwegg, K., & Bockelée-Morvan, D. 2003, *Space Science Reviews*, 106, 139
- Arpigny, C., Jehin, E., Manfroid, J., Hutsemékers, D., Schulz, R., Stüwe, J. A., Zucconi, J.-M., & Ilyin, I. 2003, *Science* 301, 1522
- Bensch, F., Bergin, E. A., Bockelée-Morvan, D., Melnick, G. J., & Biver, N. 2004, *ApJ*, 609, 1164
- Binet, L., & et al. 2004, *ASSL Vol. 305: Astrobiology: Future Perspectives*, 333
- Biver, N., et al. 1999, *AJ*, 118, 1850
- Biver, N., et al. 2002a, *Earth Moon and Planets*, 90, 323
- Biver, N., et al. 2002b, *Earth Moon and Planets*, 90, 5
- Biver, N., et al. 2005a, *A&A*, submitted
- Biver et al. 2005b, Abstract, Asteroids, Comets and Meteors 2005 IAU Symp. 229
- Biver, N., et al. 2005c, AAS/Division for Planetary Sciences Meeting Abstracts, 37,
- Blake, G. A., Qi, C., Hogerheijde, M. R., Gurwell, M. A., & Muhleman, D. O. 1999, *Nature*, 398, 213
- Bockelée-Morvan, D., et al. 2000, *A&A* 353, 1101
- Bockelée-Morvan, D., Gautier, D., Hersant, F., Huré, J.-M., & Robert, F. 2002, *A&A*, 384, 1107
- Bockelée-Morvan, D., Crovisier, J., Mumma, M. J., & Weaver, H. A. 2004, in *Comets II*, Univ. Arizona Press, 391
- Bockelée-Morvan, D. et al. 2005a, *A&A*, in preparation
- Bockelée-Morvan et al. 2005b, Abstract, Asteroids, Comets and Meteors 2005 IAU Symp. 229
- Canaves, M. V., De Almeida, A. A., Boice, D. C., & Sanzovo, G. C. 2002, *Earth Moon and Planets*, 90, 335
- Charnley, S. B., Rodgers, S. D., Butner, H. M., & Ehrenfreund, P. 2002, *Earth Moon and Planets*, 90, 349
- Clairemidi, J., Bréchnignac, P., Moreels, G., & Pautet, D. 2004, *Plan.Sp.Sci.*, 52, 761
- Clemett, S. J., Maechling, C. R., Zare, R. N., Swan, P. D., & Walker, R. M. 1993, *Science*, 262, 721
- Crovisier, J. 2004, *ASSL Vol. 305: Astrobiology: Future Perspectives*, 179
- Crovisier, J., Colom, P., Gérard, E., Bockelée-Morvan, D., & Bourgois, G. 2002, *A&A*, 393, 1053
- Crovisier, J., Leech, K., Bockelée-Morvan, D., Brooke, T. Y., Hanner, M. S., Altieri, B., Keller, H. U., & Lellouch, E. 1997, *Science*, 275, 1904
- Crovisier, J., Bockelée-Morvan, D., Colom, P., Biver, N., Despois, D., Lis, D. C., & the Team for target-of-opportunity radio observations of comets 2004a, *A&A* 418, 1141
- Crovisier, J., Bockelée-Morvan, D., Biver, N., Colom, P., Despois, D., & Lis, D. C. 2004b, *A&A* 418, L35
- Crovisier, J., et al. 2005, AAS/Division for Planetary Sciences Meeting Abstracts, 37,
- Despois, D., Cottin, H. 2005, in "Lectures in Astrobiology I", eds. Gargaud, Barbier, Martin, Reisse, Springer, 289
- Ehrenfreund, P., Charnley, S. B., & Wooden, D. 2004, in *Comets II*, Univ. Arizona Press, 115
- Fegley, B. Jr., 1993 in *The Chemistry of Life's Origins*, Greenberg, Mendoza-Gomez and Pirronello eds., Kluwer, p. 75
- Feldman, P. D., Weaver, H. A., A'Hearn, M. F., Festou, M. C., McPhate, J. B., & Tozzi, G.-P. 1999, AAS/Division for Planetary Sciences Meeting Abstracts, 31,
- Feldman, P. D., Cochran, A. L., & Combi, M. R. 2004, in *Comets II*, Univ. Arizona Press, 425
- Festou, M. C., Keller, H. U., & Weaver, H. A. (eds.) 2004, *Comets II*, Univ. Arizona Press
- Fomenkova, M. N. 1999, *Space Science Reviews*, 90, 109
- Fray, N., Bénilan, Y., Cottin, H., Gazeau, M.-C., Minard, R. D., & Raulin, F. 2004, *Meteoritics and Planetary Science*, 39, 581
- Fray N., Bénilan Y., Cottin H., Gazeau M.-C., Crovisier J. 2005, *Plan.Sp.Sci.*, 53, 1243
- Hanner, M. S., & Bradley, J. P. 2004, in *Comets II*, Univ. Arizona Press, 555
- Henry, F. 2003, Ph.D. Thesis, Paris

- Henry, F., Bockelée-Morvan, D., Crovisier, J., & Wink, J. 2002, *Earth Moon and Planets*, 90, 57
- Hirota, T., Yamamoto, S., Kawaguchi, K., Sakamoto, A., & Ukita, N. 1999, *ApJ*, 520, 895
- Hollis, J. M., Lovas, F. J., Jewell, P. R., & Coudert, L. H. 2002, *ApJ(Letters)* 571, L59
- Huebner, W. F., Keady, J. J., & Lyon, S. P. 1992, *Astr.Sp.Sci.*, 195, 291
- Iro, N., Gautier, D., Hersant, F., Bockelée-Morvan, D., & Lunine, J. I. 2003, *Icarus*, 161, 511
- Irvine, W. M., et al. 1998, *Nature*, 393, 547
- Irvine, W. M., Senay, M., Lovell, A. J., Matthews, H. E., McGonagle, D., & Meier, R. 2000, *Icarus*, 143, 412
- Irvine, W. M., Schloerb, F. P., Crovisier, J., Fegley, B., & Mumma, M. J. 2000, *Protostars and Planets IV*, Univ. Arizona Press, 1159
- Irvine, W. M., Bergman, P., Lowe, T. B., Matthews, H., McGonagle, D., Nummelin, A., & Owen, T. 2003, *Origins of Life and Evolution of the Biosphere*, 33, 609
- Jackson, W. M., Halpern, J. B., Feldman, P. D., & Rahe, J. 1982, *A&A*, 107, 385
- Jackson, W. M., Scodinu, A., Xu, D., & Cochran, A. L. 2004, *ApJ(Letters)*, 607, L139
- Jewitt D.C., Matthews, H.E., Owen, T., Meier, R., 1997 *Science*, 278, 90
- Kawakita, H., Watanabe, J.-I., Furusho, R., Fuse, T., Capria, M. T., De Sanctis, M. C., & Cremonese, G. 2004, *ApJ*, 601, 1152
- Keller, H.U., Jorda, L., Kuppers, M. et al. 2005, *Science* 2005 0: 1119020
- Kress, M., Tielens, A., & Frenklach, M. 2004, 35th COSPAR Scientific Assembly, 3692
- Lecacheux, A., et al. 2003, *A&A*, 402, L55
- Lis, D. C., et al. 1997, *Icarus*, 130, 355
- Lisse, C. M., van Cleve, J., Fernandez, Y. R., & Meech, K. J. 2005, *IAU Circ.* 8571, 2
- Lovell, A. J. 1999, Ph.D. Thesis,
- Magee-Sauer, K., Dello Russo, N., DiSanti, M. A., Gibb, E., & Mumma, M. J. 2002, *Bulletin of the American Astronomical Society*, 34, 868
- Malfait, K., Waelkens, C., Waters, L. B. F. M., Vandenbussche, B., Huygen, E., & de Graauw, M. S. 1998, *A&A*, 332, L25
- Manfroid, J., Jehin, E., Hutsemékers, D., Cochran, A., Zucconi, J.-M., Arpigny, C., Schulz, R., & Stüwe, J. A. 2005, *A&J*, 432, L5
- Meech, K. J., Ageorges, N., A'Hearn, M. F. et al. 2005, *Science* 2005 0: 1118978
- Moreels, G., Clairemidi, J., Hermine, P., Brechignac, P., & Rousselot, P. 1994, *A&A* 282, 643
- Mousis, O., Gautier, D., Bockelée-Morvan, D., Robert, F., Dubrulle, B., & Drouart, A. 2000, *Icarus*, 148, 513
- Rodgers, S. D., & Charnley, S. B. 2001, *MNRAS*, 323, 84
- Rolfe, E. J., & Battrick, B. 1987, ESA SP-278: Diversity and Similarity of Comets
- Smith, A. M., Stecher, T. P., & Casswell, L. 1980, *ApJ*, 242, 402
- Veal, J. M., et al. 2000, *AJ*, 119, 1498
- Ziurys, L. M., Savage, C., Brewster, M. A., Apponi, A. J., Pesch, T. C., & Wyckoff, S. 1999, *ApJ(Letters)*, 527, L67