Chapter 1

THE MOLECULAR COMPLEXITY OF COMETS

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Abstract By delivering prebiotic molecules to the Earth, comets could have played a role in the early phases of the development of life on our planet. In order to explore this possibility, we present here an assessment of the molecular content of comets. The current methods of investigations — by both in situ analysis and remote sensing — are reviewed. The present status of our knowledge of the composition of cometary ices is reviewed. We probably now know most of the main components, but we still have a very partial view of the minor ones. A large diversity of composition from comet to comet is observed, so that no "typical comet" can be defined. No clear correlation between the composition and the region of formation of the comets and their subsequent dynamical history can yet be established. A crucial cometary component, both for cometary coma chemistry and for the possible delivery of organics to the Earth, is the (semi-)refractory high molecular-mass organic material present in grains. From the advent of new instrumentation, we can expect the detection of many new molecular species in future bright comets. However, the identification of really complex molecules will need in situ analysis or the return to Earth of nucleus samples.

Keywords: Astrobiology, comet, molecule, space mission, spectroscopy

1. Introduction

To understand how life could have appeared on Earth is a formidable project. We are only beginning to gather the pieces of the puzzle. One of them is the assessment of the chemical conditions in the early Earth. In this respect, the fall of comets could have played a crucial role by injecting organic — and possibly prebiotic — molecules (Oró 1961; Thomas et al. 1997). This possibility, which has been the object of passionate debates for a long time, relies on the answers to two questions:

- Do indeed comets contain molecules of a prebiotic interest?

- Could such molecules survive cometary impacts on Earth?

The object of the present Chapter is to try to answer the first question. Our knowledge of the chemical nature of cometary volatiles has considerably evolved during the last two decades with the advent of space exploration and of modern spectroscopic techniques. About two dozen species are now known, including the main constituents (H_2O, CO, CO_2, CH_4, CH_3OH, H_2CO, NH_3, H_2S)[1], and a number of trace species. We note that several species among identified molecules are "building blocks" for prebiotic molecules, i.e. they may react spontaneously in liquid water to form molecules like amino acids or nucleic acids. These are H_2CO, HCN, HC_3N, CH_3CN... Fortunately, comets have not evolved, so that the study of comets nowadays informs us on the nature of comets which could have seeded the Earth in the early times.

To the second question, Nature has offered opposite answers. On the one hand, the collision of comet Shoemaker-Levy 9 on Jupiter in July 1994 was followed by a surge of new molecular species in the atmosphere of the giant planet. These species were not the original molecules contained in the comet, rather the result of intense chemical processing of cometary material with the planetary atmosphere (Crovisier 1996; Lellouch 1996). The memory of the chemical content of the comet was lost. On the other hand, the analysis of meteorites — especially of carbonaceous chondrites, which are presumed to be akin to cometary nuclei — does show the presence of many organic molecules which survived the impact (Berzelius 1834; Botta & Bada 2002).

Next section will explain the various techniques (remote sensing or in situ analysis) which can be used to probe the chemical composition of comets. Section 3 will assess our present knowledge of the molecular content of comets, with an accent on molecular complexity and on the comet-to-comet variations. Section 4 will deal with future prospects: Which molecules could we expect to detect with new techniques?

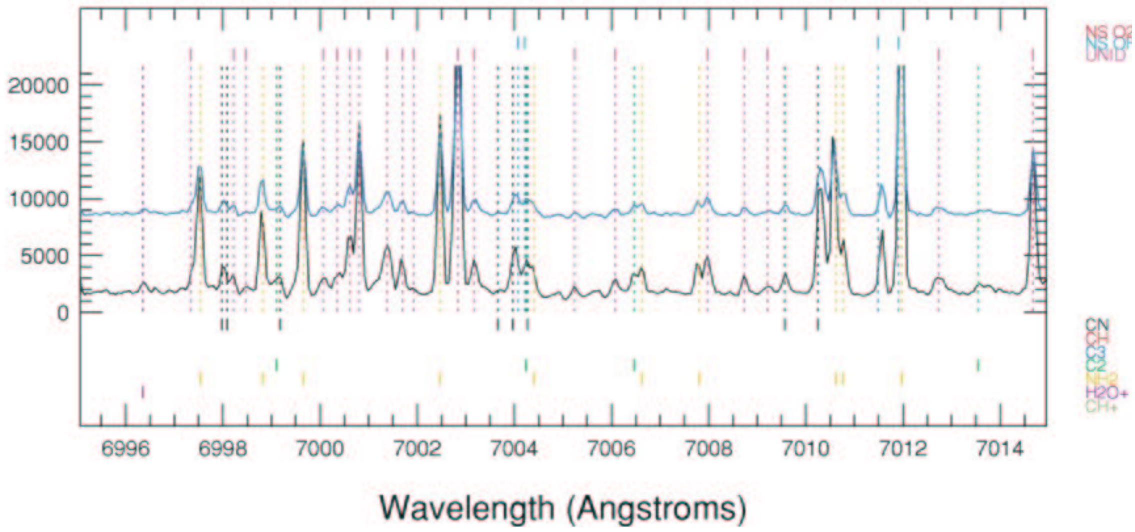

Figure 1.1. Excerpt of the high-resolution spectrum of comet 122P/de Vico. One can see lines of CN, C_2, NH_2, and many unidentified features. (Adapted from Cochran & Cochran 2002.)

2. The chemical composition of comets: methods of investigation

Awaiting for the results of ongoing or future space missions with in situ analyses and the return of samples from cometary nuclei, information of the chemical composition of cometary ices can only be obtained from remote sensing of the coma formed by matter released during cometary activity. Volatile molecules coming from the sublimation of cometary ices — the so-called *parent molecules* — are readily photo-processed to form secondary products, radicals, ions, atoms — the so-called *daughter molecules*.

2.1 Visible spectroscopy

Visible spectroscopy has been at work in astronomy for nearly one century and a half. Its application to comets (Fig. 1.1) is intimately linked to the beginnings of astrophysics and to laboratory spectroscopy. It took time to identify the features... Only dissociation or ionization products can be observed in this spectral domain, so that guesses had to

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[1]Listed here are the species with abundances $\geq 1\%$ relative to water.

be made to infer what are their parent molecules. In the 1950's, from the observation of daughter molecules (CH, CO^+, NH, NH_2, OH, C_2, CN), only a handful of parents (H_2O, CO_2, CH_4, NH_3) could be proposed (e.g., Whipple, 1950). These guesses were basically right! However, it was not yet possible to have access to the actual complexity of the composition of cometary ices. One had to wait for the development of spectroscopy in other domains to directly identify parent molecules.

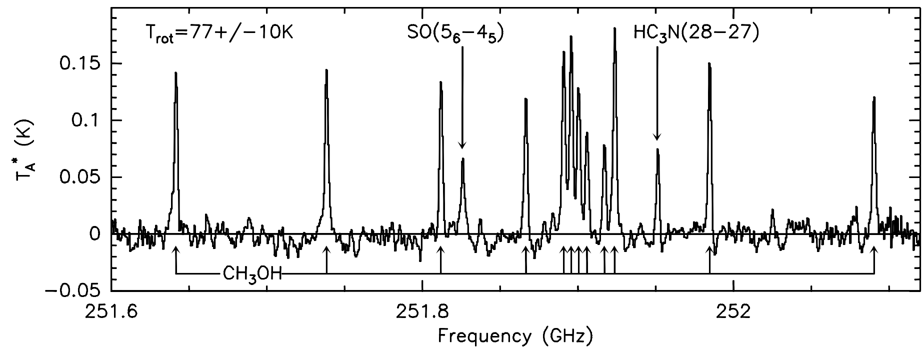

Figure 1.2. A millimetric spectrum of comet C/1995 O1 (Hale-Bopp) observed at the *Caltech Submillimeter Observatory* on 21 March 1997. This spectrum is chosen for its complexity. It covers a total frequency range of about 1.2 GHz (in this receiver setup, the spectrum is a mixture of the lower side-band — whose frequency scale is indicated in the figure — and of the upper side-band which is shifted by 5 GHz). The spectrum shows a series of lines of methanol for which the corresponding rotational temperature is indicated, and the first observations of SO and HC_3N (at 244.700 GHz in the upper side-band) in a comet. (From Lis et al. 1999.)

2.2 Radio and infrared spectroscopy

In the last two decades, radio and infrared spectroscopy (and to a lesser extent ultraviolet spectroscopy) led to the identification of about two dozen cometary volatiles (Figs 1.2 & 1.3). Radio spectroscopy (rotational lines) is more sensitive than IR spectroscopy (vibrational bands) for species with a significant dipolar moment[2]. Non-polar species (such as symmetric hydrocarbons) can only be investigated by IR spectroscopy.

[2]Species with abundances as small as 2×10^{-4} relative to water were observed in the radio spectra of comet Hale-Bopp. Species observed in the infrared had abundances of several 10^{-3}.

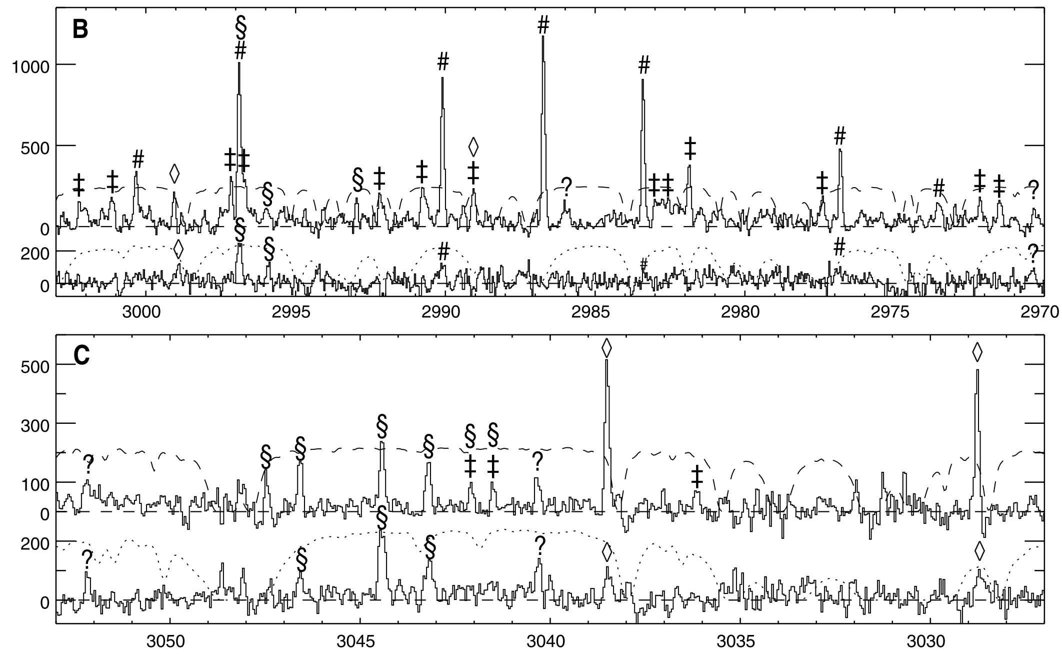

Figure 1.3. Excerpts of the infrared spectra of comets C/1999 H1 (Lee) (top of each frame) and C/1999 S4 (LINEAR) (bottom), observed with the Keck telescope. One can see lines of CH_3OH (‡), C_2H_6 ($\sharp$), CH_4 ($\diamond$) and OH (§). Note the presence of several unidentified lines (?). The dashed and dotted lines show telluric transmission. (Adapted from Mumma et al. 2001.)

2.3 Surface reflectance spectroscopy

Cometary nuclei are very dark (albedo ≈ 0.03) and red (but not as red as some Centaurs and Kuiper belt objects). Reflectance spectroscopy of cometary nuclei could inform us on the composition of their surface. Such an observation at a large distance is, however, a formidable challenge because of the weakness of the signal, which could be dominated by the much more intense emission by the dust coma when the comet is active. It was successfully applied to the investigation of large Kuiper belt objects and Centaurs (de Bergh 2004). It could also be performed on the nucleus of comet 19P/Borrelly during its fly-by by *Deep Space 1*. Surprisingly, no water ice signature was revealed. The near-IR spectrum was featureless, except for an unidentified feature at 2.39 μm (Soderblom et al. 2004; Fig. 1.4).

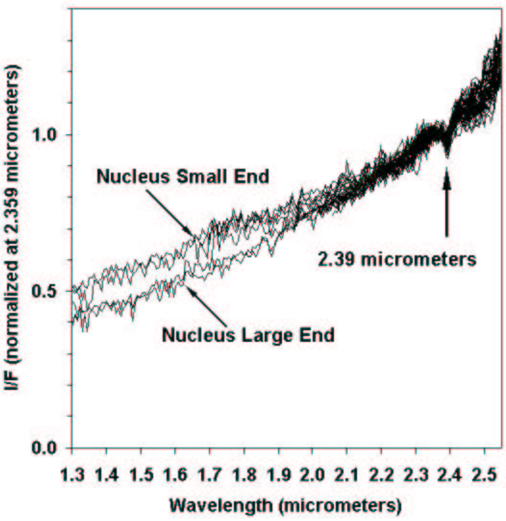

Figure 1.4. Near-infrared spectra of the nucleus of comet 19P/Borrelly observed by *Deep Space 1*. Note the absence of spectral features, except for an unidentified absorption at 2.39 μm. (From Soderblom et al. 2004.)

2.4 Mass spectroscopy

In situ mass spectroscopy is a very powerful mean of investigation. However, up to now it was only exercised in comet Halley (Altwegg et al. 1999; Eberhardt et al. 1999; Fig. 1.5). It was then seriously hampered by mass ambiguity due to its limited spectral resolution. The *ROSINA* instrument designed for *Rosetta* (Balsiger et al. 2003) has a much better resolution than the mass spectrometers of *Giotto*.

Another problem is that this technique is only sensitive to ions — either ions already present in the coma, or coming from the ionization or protonization of cometary neutrals by the apparatus. Thus chemical modelling is necessary to retrieve information on the parent molecules from the ionized species effectively observed by the mass spectrometer. This problem may be as difficult as the guess of parents from the observed daughters mentioned above about visible spectroscopy. It may be pointed out that in the interpretations of the mass spectroscopy data from comet Halley, most of the *correct* identifications and abundance determinations were made a posteriori, after the way had been cleared by spectroscopic remote sensing.

The time-of-flight mass spectrometer *PUMA* on board *VEGA 1* revealed several high molecular mass compounds in comet Halley's dust grains (Kissel & Krueger 1987; also Kissel et al. 1997), that the authors

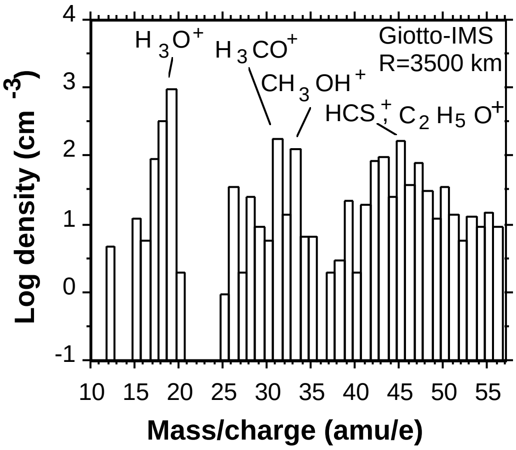

Figure 1.5. The mass spectrum of gas observed in 1P/Halley by the *IMS* instrument. (From Altwegg et al. 1999.)

attributed to specific organic species such as adenine, pyrimidine, and their compounds. These highly speculative hypotheses will have to be confirmed in the future using more selective identification techniques.

2.5 Chromatography

Chromatography is another powerful in situ mean of investigation, especially when associated with mass spectroscopy. Space gas chromatography was successfully used on Mars (*Viking* probes) and Venus (*Pioneer-Venus*, *Venera* and *Vega* probes). It will investigate the atmosphere of Titan (*Cassini-Huygens*). It will be used on the *Rosetta* lander to probe the nucleus of comet 67P/Churyumov-Gerasimenko (the *COSAC* experiment: Rosenbauer et al. 1999; Thiemann et al. 2001; Szopa et al. 2003; Fig. 1.6). Szopa et al. estimate that species with abundances 10^{-5}–10^{-6} relative to water could be detected with *COSAC* (for those species that can be sampled with the dedicated chromatographic columns). Semi-refractory species (e.g. glycine) will not be released; they could be studied by pyrolysis and derivatisation. Chirality could be investigated with specific chromatographic columns.

2.6 Fetching cometary material

Ultimately, the return of a sample of cometary nucleus would allow us to perform its study at leisure in Earth laboratories. Several scenarios of *Comet Nucleus Sample Return* missions have been studied and

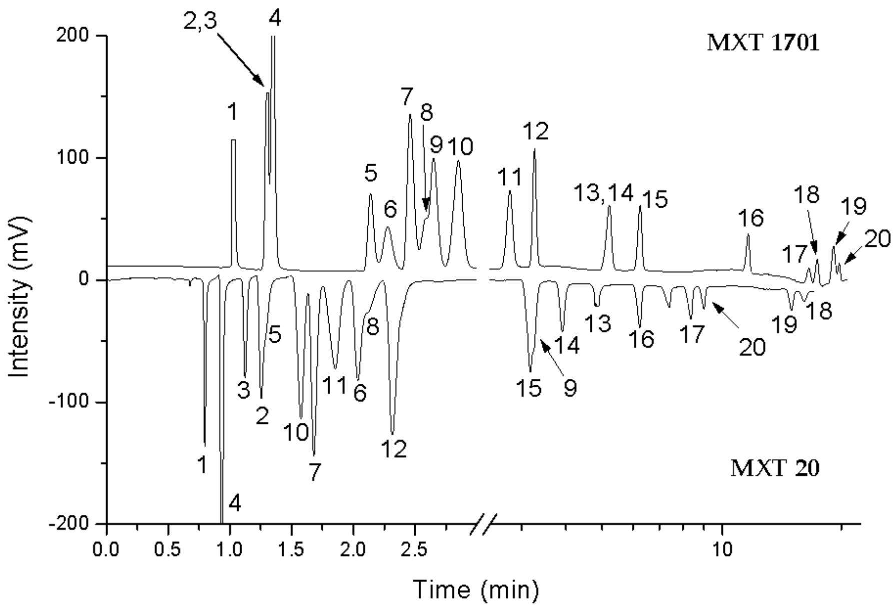

Figure 1.6. Example of calibration chromatograms obtained with two different columns in preparation of the *COSAC* experiment on the lander of *Rosetta*. The peaks correspond to 1 = nitrogen, 2 = water, 3 = methanol, 4 = benzene, 5 = formamide, 6 = pyridine, 7 = toluene, 8 = pentanol, 9 = octane, 10 = ethyl benzene, 11 = m-xylene, 12 = p-xylene, 13 = cyclohexanone,14 = o-xylene, 15 = nonane, 16 = propyl benzene, 17 = trimethyl benzene, 18 = decane, 19 = p-cymene, 20 = indene. (From Szopa et al. 2003.)

proposed[3]. There is presently no firmly scheduled mission to return a genuine sample of cometary nucleus, due to complexity and cost. The *Stardust* mission (Brownlee et al. 1997) towards comet 81P/Wild 2 (fly-by in January 2004) is expected to return samples of dust grains to Earth in January 2006. These grains will not have retained any icy component. But perhaps they will still contain organic refractories — they could be similar to some interplanetary dust particles collected in the Earth stratosphere which are believed to be of cometary origin.

2.7 Home delivery of cometary material

Why bother going at a comet nucleus and back to fetch samples, or studying it painstakingly at distance? Large amounts of cometary

[3]Among them, earlier versions of *Rosetta* and *Champollion* (an aborted NASA mission similar to *Rosetta*).

Table 1.1. Molecules, radicals, ions and atoms observed in cometary comae, with their means of detection: radio (rad.), infrared (IR), visible (vis.), ultraviolet (UV) spectroscopy, or mass spectrometry[a] (MS).

	rad.	IR	vis.	UV	MS		rad.	IR	vis.	UV	MS
H_2O	x	x			x	N				x	
H_2O^+			x			N_2^+			x		
H_3O^+	x					NH_3	x	x			x
OH	x	x		x		NH			x		
H			x	x		NH_2		x	x		
H_2				x		HCN	x	x			x
O			x	x		HNC	x				
O^+				x		CN	x	x	x		
CO	x	x		x	x	CH_3CN	x				x
CO_2		x			x	HC_3N	x				
CO^+	x		x	x		HNCO	x				
CO_2^+			x			NH_2CHO	x				
C				x		H_2S	x				x
C_2		x	x			CS	x			x	
C_3			x			SO	x				
CH_4		x				SO_2	x				
C_2H_2		x			x	OCS	x	x			
C_2H_4					x	H_2CS	x				
C_2H_6		x			x	NS	x				
C_4H_2		x				S_2				x	
CH		x	x			S				x	
CH^+			x			Na			x		
CH_2					x	K			x		
H_2CO	x	x				Ar				?	
HCO^+	x					metals[b]			x		
CH_3OH	x	x			x						
HCOOH	x										
CH_3CHO	x										
$HCOOCH_3$	x										

[a] The species detected by mass spectroscopy of comet 1P/Halley are taken from the compilation of Altwegg et al. 1999 (Table II); also listed as "probably detected" were CS, OCS, CH_3CHO, C_3H_2 and C_2H_5CN (ibid., Table III).
[b] Various metal atoms were only observed in the sungrazing comet C/1965 S1 (Ikeya-Seki).

material are continuously delivered to Earth. This is the very mechanism which is the motivation of the present Chapter, albeit a delivery rate much lower nowadays than it was in the early times!

Meteor showers are attributed to the shedding of dust by cometary nuclei. The spectroscopy of meteoroids, although a challenging obser-

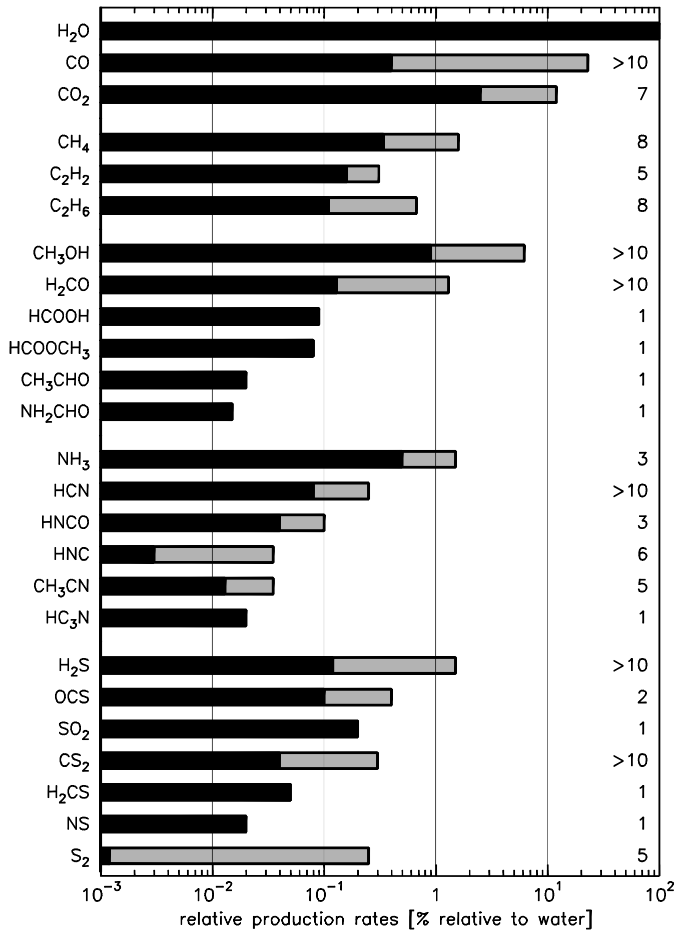

Figure 1.7. Relative production rates of cometary volatiles and their comet-to-comet variations[a]. These rates are believed to trace the relative abundances in cometary ices. The grey part of each bar indicates the range of variation from comet to comet. On the right, the number of comets in which the species was detected is indicated. (From Bockelée-Morvan et al. 2005.)

[a] Some species reported in this figure appear to come (in part) from extended sources, not directly from nucleus ices (See Section 3.3). CS_2 is not observed directly: its production rate is estimated from its daughter CS. NS is a radical for which no plausible parent has yet been proposed. The origin of S_2 is not well understood.

vation, would inform us on their chemical composition (e.g., Abe et al.

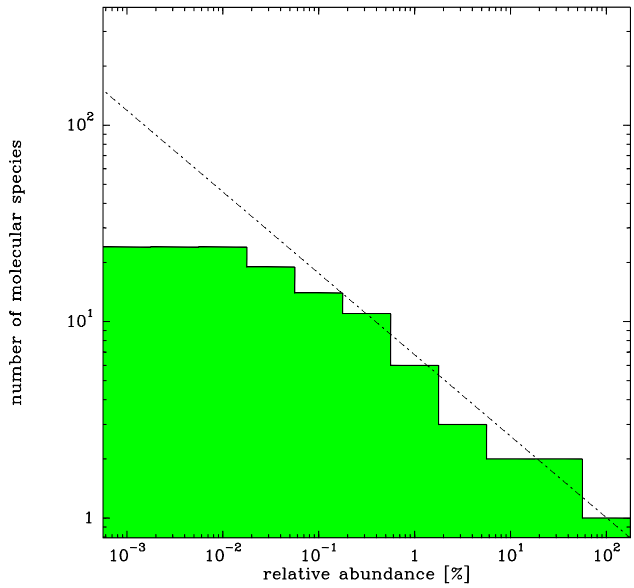

Figure 1.8. The cumulative histogram of molecular parent species detected in comet Hale-Bopp with production rates (in percent relative to water) larger than a given value. The observed distribution departs from the true distribution for the less abundant species because of sensitivity issues. The dashed line is a guess of the true distribution. (From Bockelée-Morvan & Crovisier 2002.)

2002). IDP's collected in the upper atmosphere as well as micrometeorites are supposed to contain a significant fraction of cometary dust particles (Molster 2004).

In situ analysis and the study of returned samples of cometary dust will provide ground truth for evaluating the relation between chondritic porous IDP's and cometary material. It has been argued for a long time whether some meteorites (among CI and CM carbonaceous chondrites) could actually be parts of cometary nuclei (Campins & Swindle 1998; Lodders & Osborne 1999), but direct clues are still lacking.

3. The chemical composition of comets: present status

Although this is still small number statistics (for both the number of comets investigated and the number of molecules detected), our knowledge of the composition of cometary material is rapidly expanding. It is

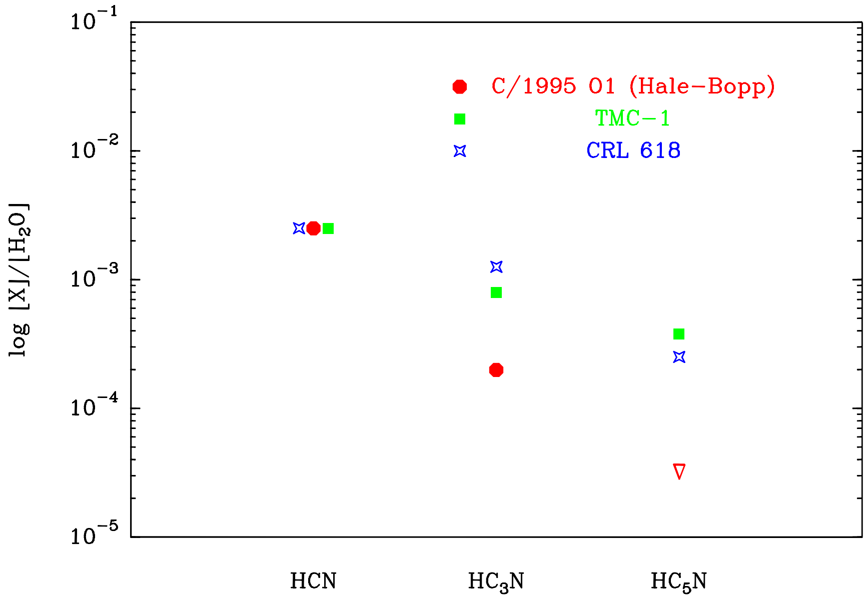

Figure 1.9. The relative abundances of linear cyanopolyynes in comet Hale-Bopp (Bockelée-Morvan et al. 2000; Crovisier et al. 2004), in the dark cloud TMC–1 (Irvine et al. 1987) and in the proto-planetary nebula CRL 618 (Cernicharo et al. 2001). For the comet, the abundances are plotted relative to water and the triangle indicates an upper limit. For the interstellar sources, the abundances are normalized to that of HCN.

the topic of several recent reviews (Crovisier 1998; Crovisier & Bockelée-Morvan 1999; Bockelée-Morvan et al. 2000; Irvine et al. 2000; Despois et al. 2002; Bockelée-Morvan et al. 2005). It is summarized in Fig. 1.7. Detailed information is only available for a very small number of comets (1P/Halley, C/1996 B2 (Hyakutake), C/1995 O1 (Hale-Bopp), C/1999 H1 (Lee), C/1999 S4 (LINEAR), 153P/Ikeya-Zhang). About 7 species were observed in comet Hale-Bopp only.

3.1 Molecular complexity

Altogether, 44 molecular species, radicals or molecular ions are identified in comets (Table 1.1). This is to be compared with about 130 species (excluding isotopologues) detected in the interstellar medium. However, we must have in mind that these *interstellar molecules* are not all detected in a single source[4].Among them are 25 stable volatile molecules, likely to have sublimated from nucleus ices (Fig. 1.7), but upper limits are set on many other species[5].

Fig. 1.8 shows the cumulative distribution of the number N of identified cometary parent molecules as a function of their relative production rates X observed in comet Hale-Bopp[6]. We probably now know the most abundant species down to a level of about 1%. The distribution is obviously stalling for abundances $< 0.1\%$, which reveals that less abundant (trace) species are still sparsely known at this level. The dashed line (which corresponds to a power law $N \propto X^{-0.4}$) is a rash extrapolation of the distribution to small abundances. If realistic, it would imply we should expect ≈ 100 species with abundances $> 0.001\%$ relative to water (isotopologues are excluded from this study).

Cometary volatiles have very different equilibrium sublimation temperatures[7]. Thus, fractionation at sublimation may occur, so that the observed relative production rates of cometary volatiles do not directly correspond to their relative abundances in cometary ices (Huebner & Benkhoff 1999; Biver et al. 2002a). For instance, the $[CO]/[H_2O]$ ratio is observed to increase with heliocentric distance, due to the higher volatility of CO; no water is produced at $r_h > 4$ AU whereas CO was still observed up to 15 AU in comet Hale-Bopp (and could explain alone cometary activity at these distances). But in a high sublimation regime at $T > 180$ K dominated by water, such as that which occurs at $r_h < 1$ AU, all volatiles sublime alike and little fractionation is expected. Another object of concern is the possibility of chemical synthesis: could some of the observed trace species be the result of chemical processes rather than coming from nucleus ices? According to the calculations of Rodgers & Charnley (2001), this is not the case, even in a very productive comet such as Hale-Bopp. This is due to the cold temperature of the coma, its low ionisation state, and the short time spent by molecules in the collision zone.

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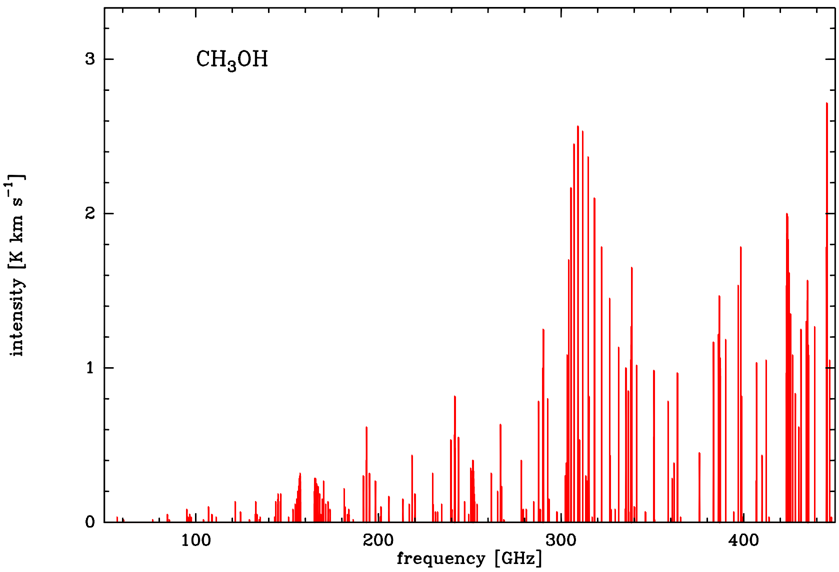
[4]For instance, the longest carbon-chain molecules are only observed in dark clouds (TMC–1); complex CNO molecules are only observed in hot cores (Galactic centre, Orion IRc2); some hydrocarbons were only detected in circumstellar envelopes (IRC+10216 or CRL 618). (See e.g., Millar 2004.)

[5]For instance, ketene (CH_2CO) $< 0.03\%$, ethanol (C_2H_5OH) $< 0.1\%$, glycine (NH_2CH_2COOH) $< 0.15\%$, dimethyl ether (CH_3OCH_3) $< 0.5\%$, cyanodiacetylene (HC_5N) $< 0.003\%$, methanimine (CH_2NH) $< 0.03\%$ relative to water (Crovisier et al. 2004).

[6]It would be interesting to plot similar histograms for the relative molecular abundances in typical interstellar medium objects, or for biological bodies, or for those resulting from chemical models, to see whether a power law $N \approx X^{-\alpha}$ is emerging with a similar or different exponent.

[7]The sublimation temperatures range from 25–30 K for CO and CH_4, to 70–100 K for CO_2, NH_3, HCN, CH_3OH, up to 150–180 K for H_2O.



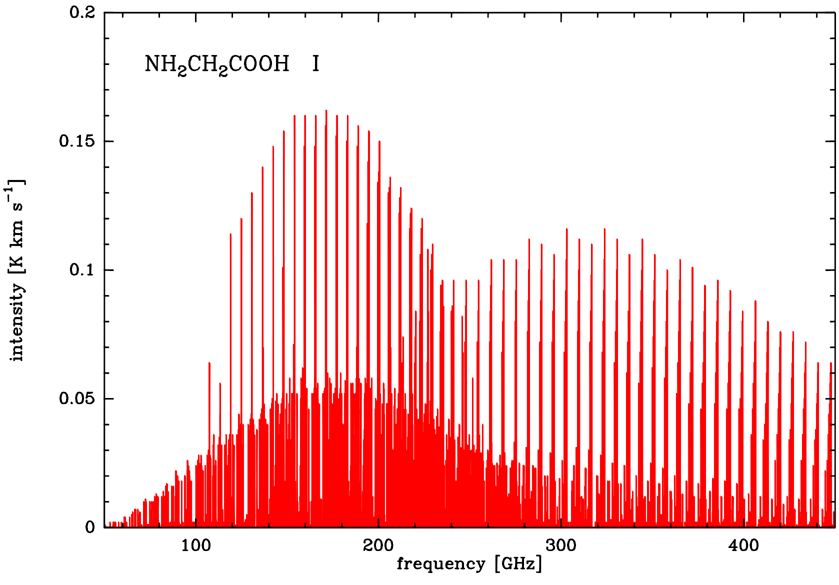


Figure 1.10. The microwave spectra expected for cometary methanol (top) and glycine (conformer I, bottom). They were computed for the following conditions: comet at 1 AU from Sun and Earth, observed with a 30-m telescope, coma at a temperature of 70 K and 0.8 km/s expansion velocity, molecular production rates of 10^{28} s^{-1} for each species. Note the much more intense lines of methanol. Many lines of CH_3OH were observed in several comets. Glycine is still undetected. Molecular data are taken from the JPL molecular data base.

Obviously, abundances decrease with increasing molecular complexity. Fig. 1.9 shows that the relative abundance of cometary cyanopolyynes ($HC_{2n+1}N$) decrease more rapidly than in interstellar clouds[8]. From the upper limits determined in comet Hale-Bopp (Crovisier et al. 2004), the ratio [ethanol]/[methanol] is also rather low ($< 1/25$). This may not be the same for all cometary molecules in *homologous series*. For instance, [ethane]/[methane], now observed in several comets (Gibb et al. 2003), is close to one[9].

Cyanopolyynes are simple, linear molecules with a strong dipolar moment. Therefore, their radio spectra consist in a simple series of strong lines. They can be observed with very low abundances. In contrast, the upper limits on complex molecular species are not good. For instance the upper limit is only 0.15% in number relative to water for glycine[10](Crovisier et al. 2004). This is due to the high value of the partition function of such molecules which have many rotational levels populated even at low temperatures, which have additional degrees of freedom due to internal rotation, and which may have several low-energy conformers. Their spectra are complex, with a forest of lines (Fig. 1.10). Such species should be searched for by in situ analysis rather than by remote sensing.

3.2 Chemical diversity

According to the current cosmogonic theories, all comets formed at the very beginning of the history of the Solar System, from accretion of planetesimals in the proto-planetary disc beyond the *snow line*[11]. But they followed different fates, depending on where they were formed. Beyond Neptune, comets constituted part of the Kuiper belt. In the inner Solar System, newly formed comets in the Jupiter–Neptune region were readily ejected by gravitational interaction with the giant planets: they either left the Solar System, or formed a spherical, distant cloud, the Oort cloud.

There are thus two reservoirs of comets. Further perturbations provoke changes of orbits that may bring back comets from both reservoirs

[8]Cronin (1998) has noted that for carboxylic acids analysed in meteorites, the abundance decreases by $\approx 60\%$ for each additional C-chain atom.
[9]In this specific case, this could be due to a difference of volatility (sublimation equilibrium temperatures of 31 K for CH_4, 44 K for C_2H_6) rather than to a chemical effect.
[10]This corresponds to about 0.3% in mass in nucleus ices. This is to be compared with the abundance of $\approx 10^{-5}$ in mass measured for the whole amino acids in carbonaceous chondrites (Botta and Bada 2002).
[11]The snow line is the heliocentric distance beyond which water could condense. This is ≈ 5 AU (about the Jupiter's heliocentric distance) in the present Solar System.

to the inner Solar System. Comets from the Kuiper belt give Jupiter-family comets, with short periods and low inclinations on the ecliptic plane. Comets from the Oort cloud may have all kinds of periods and random inclinations. One would expect different compositions for these two main dynamical classes of comets, depending on where they were initially formed. For instance, comets formed at large heliocentric distances in the Kuiper belt could have retained species more volatile than the Oort cloud comets.

A first attempt of a taxonomy of comets based upon their chemical composition was made by A'Hearn et al. (1995) from the relative production rates of daughter specie (OH, CN, C_2, C_3, NH). Two classes of comets were identified: *typical comets*, and *carbon-depleted comets*, on the basis of the $[C_2]/[CN]$ ratio. Half of the Jupiter-family comets appear to be carbon-depleted, whereas most of the Oort cloud comets are typical. How does this variety in relative abundances of daughters translate into variety in the abundances of parents is unknown, because of, e.g., the large number of precursors for C_2.

There is now a significant sample of comets (about twenty) for which the main volatile components (parent molecules) have been investigated. No "typical comet" could be proposed with respect to chemical composition. A large chemical diversity is revealed (radio observations: Biver et al. 2002b; infrared observations of hydrocarbons: Mumma et al. 2002; Fig. 1.7). Although the $[HCN]/[H_2O]$ ratio is fairly constant, CH_3OH, H_2CO and H_2S show large variations. Carbon monoxide is still more variable (by about a factor fo 50).

The relation of chemical composition with dynamical classes of comets and their site of formation — *Oort cloud* (long-period) comets versus *Kuiper belt* (Jupiter-family) comets — is unclear. This relation may be blurred by the fractionation in Jupiter-family comets expected from repeated passages close to the Sun. More observations are needed to increase the number of comets (especially the weaker Jupiter-family comets) and of molecules.

Of which dynamical class were the comets which seeded the Earth in the early times? Discussing the possible external delivery of water to Earth by small bodies impacts, Morbidelli et al. (2000) estimate that the Earth benefited from cometary impacts all along its formation. First, from comets from the Jupiter–Saturn region (i.e., the same comets as those which were ejected to the Oort cloud), when the Earth was still less than half its present mass. Last, from comets originating from the Uranus–Neptune region and the Kuiper belt[12].

According to Binzel et al. (2002), up to 30% of the near-Earth objects — which are objects with orbits crossing the Earth orbit and therefore likely to impact the Earth — are extinct or dormant comets[13].

3.3 The mystery of the "extended sources"

Extended sources of molecules are needed to explain the production, distribution, and evolution with heliocentric distance of cometary CO, H_2CO and HNC/HCN.

The evidences for extended sources (see review in Bockelée-Morvan & Crovisier 2002) first came from in situ exploration of 1P/Halley, then from long-slit spectroscopy in the IR and mapping in the radio (both by single dishes and interferometers). Extended sources are suggested for CO, H_2CO, HNC, OCS. The most clear-cut case is that of H_2CO, which might have no significant nuclear source at all. The most important extended source is that observed in comet Hale-Bopp, for which about half of the 20% (relative to water) production of CO was coming from the extended source (DiSanti et al. 2001). This extended source appears to have turned on at $r_h < 1.5$ AU. However, this analysis is complicated by the presence of rotating jets of CO (Henry et al. 2002) in that comet. The extended source of CO was observed to be relatively much weaker in comet C/1996 B2 (Hyakutake) (DiSanti et al. 2003) and no extended source could be found in comet 153P/Ikeya-Zhang (DiSanti et al. 2002).

Admittedly, extended sources are expected from icy grains and from the photolysis of parent molecules (CO_2, H_2CO and CH_3OH produce CO). However, the scale length observed for the extended source of CO ($\approx 10^4$ km) does not fit: it is too long for sublimating icy grains, too short for photolysed parents. Furthermore, the production of extended CO is much larger in comet Hale-Bopp than that observed for plausible CO-parents.

Such sources could be CHON refractories (or semi-refractories) and/or polymers on cometary grains. From the elemental composition[14] of the dust grains of 1P/Halley, Fomenkova (1999) estimated that $\approx$ 50% in

[12]But they estimate that the bulk of the water presently on Earth was coming from a few planetary embryos originally formed in the outer asteroid belt.

[13]*Dormant comets* are cometary nuclei which have built up a protective crust and are therefore inactive even at 1 AU. Their inner nucleus has the same composition as other comets. *Extinct comets* have exhausted their volatiles and are no longer active. They could however still contain semi-refractory CHON material.

[14]Measured by the dust-impact time-of-flight mass spectrometers *PUMA* on *VEGA* and *PIA* on *Giotto*.

mass of the grains were organic refractories. Of course, the exact composition of these organics cannot be unambiguously assessed. HCN polymers and polyoxymethylene (H_2CO polymer) have been specifically invoked. The release mechanisms of light molecules from refractories is still ill-understood. Laboratory studies are necessary, such as those made on the photo- and thermo-degradation of polyoxymethylene by Cottin et al. (2001). The steep variation with heliocentric distance of the production of molecules from extended sources rather suggests that a temperature-dependent mechanism, such as thermo-degradation, is at work.

The nature of cometary refractory organics will be investigated in situ by *Stardust* and *Rosetta*. But it is dubious that the true composition of such complex species could be revealed. After all, even terrestrial material such as tholins, kerogen or caramel is not so well chemically characterized from laboratory analyses.

Being less sensitive to destruction during impacts, such organics could have been a significant source of prebiotic material to the early Earth!

4. Future prospects: sensitivity and confusion issues

A gain in sensitivity is clearly needed to make significant progresses, but the ultimate limit will be provided by the confusion limit in the spectra.

4.1 Confusion in cometary spectra

4.1.1 Confusion in radio spectra. Avery (1987) analysed the radio spectra of interstellar medium objects He found that the number of lines with antenna temperature between T_A and $T_A + \Delta T_A$ follows the law[15] $T_A^{-2}\Delta T_A$. A similar law might apply to cometary spectra.

A first advantage of comets over interstellar sources is the small width of their molecular lines: 2 km s^{-1}, which is to be compared to interstellar medium objects: 50 km s^{-1} for the Galactic centre, 5 km s^{-1} for the Orion IRc2 hot core, 30 km s^{-1} for the circumstellar envelope IRC+10216, and 10 km s^{-1} for the bipolar flow L 1157). Cold dark clouds (e.g., TMC–1) have narrow lines comparable to those of comets (or even narrower), but their gas-phase content is not so rich because most molecules are frozen into ices. Another advantage of comets is

[15] Note that this law does not converge when integrated to low T_A's: it leads to an infinite continuum (Olbers' paradox). If all species had similar spectroscopic properties, this would convert into a similar law for the column densities of species; the integration would similarly lead to an infinite total column density.

the relatively colder temperature of their molecules (≈ 100 K for comet Hale-Bopp at $r_h \approx 1$ AU — less for less productive comets or comets at larger heliocentric distances), which is to be compared with $T_{rot} \approx 250$ K in Orion IRc2. More than a factor of ten more lines (and thus ten times more species) could ultimately be detected in comets before being limited by confusion.

4.1.2 Confusion in infrared spectra. The *VIRTIS* instrument (Coradini et al. 1998) designed for *Rosetta* has a limited resolution, similar to that of the *ISO* short-wavelength spectrometer ($R \approx 2000$). This barely allows us to resolve the rotational structure of the vibrational bands. The number of detectable species will be severely limited given this resolution. Could deuterated species be detectable (HDO, CH_3D... Gibb et al. 2002; Kawakita et al. 2003) with such instrumentation? Examples of what could be confused infrared spectra is given by the Earth atmosphere spectra obtained by limb sounding with the *ATMOS* experiment ($R \approx 500\,000$; Farmer & Norton 1989). The cometary spectra recently measured from the ground by *IRTF/CSHELL* and *Keck/NIRSPEC* have a much higher resolution ($R \approx 20\,000$), but telluric lines may be a problem (Mumma et al. 2003).

4.1.3 Confusion in chromatograms and mass spectra. For an experiment such as *COSAC*, confusion caused by coelution also limits the number of species that could be detected with a single chromatographic column to about 20–30 (Fig. 1.6). At the detection limit of *COSAC* (10^{-5}–10^{-6} relative to water), one would expect more than 100 cometary species (Fig. 1.8). Confusion rather than sensitivity is thus a problem. The use of several chromatographic columns, complementary data from mass spectroscopy together with sophisticated retrieval methods (Pietrogrande et al. 2003) are needed to get the best from the data.

4.2 Unidentified lines

The numerous lines in cometary spectra which are not yet identified strongly suggest that many more species are potentially present.

The visible spectrum of comets is still far from being fully understood. For instance, in their high-resolution spectral atlas of comet 122P/de Vico, Cochran & Cochran (2002) identified 12 219 emission lines and reported no less than 4 219 unidentified lines[16] (Fig.1.1). In the far UV, the *FUSE* satellite observatory has observed several unidentified lines, presumably due to atoms or ions (Feldman et al. 2002). In the infrared, high-resolution spectra (Fig. 1.3; Mumma et al. 2003) many unidentified lines have been noted in the 3–5 μm region. Methanol is known to be the main contributor of the emission observed in the 3.2–3.5 μm region. But a definite evaluation of this contribution is still awaiting a detailed model of the methanol infrared spectrum. PAH's are probably contributing to the 3.28 μm emission feature observed in some comets. Other contributors could be CHO species, hydrocarbons, radicals or even molecular ions. Even in the radio domain, unidentified lines have been noted (Crovisier et al. 2004).

Solving these problems require further spectroscopic laboratory work and the building of comprehensive molecular data bases. This is especially the case for NH_2 in the visible and CH_3OH in the infrared: these species have so complex spectra that cometary spectra must be cleaned from their contribution to assess the presence of genuinely new species.

4.3 Future prospects

What are the future molecules to be detected? All likely simple molecules have now been detected (H_2O, CO, CO_2, NH_3, CH_4), except N_2 and O_2[17]. A similarity between the composition of cometary ices and that observed in the interstellar hot cores has been noted (Bockelée-Morvan et al. 2000). This does not necessarily mean that comets have directly incorporated unprocessed interstellar material, but that processes leading to the formation of molecules were similar in the interstellar medium and in the protosolar nebula. Going on with this analogy would suggest that further *interstellar molecules* (e.g. dimethyl ether CH_3OCH_3, acetic acid CH_3COOH, glycolaldehyde $HOCH_2CHO$, ethylene glycol $HOCH_2CH_2OH$) are to be identified in comets[18].

[16] A significant part of them could be attributed to NH_2 (M. Vervloet, *personal communication*).

[17] N_2 and O_2 do not have easily observable spectral signatures, so that no very stringent upper limit could be put on their abundances (but these species, which are very volatile, may have not been retained in cometary ices). The presence of N_2 has been suggested from the identification of a N_2^+ band in the near UV. However, this identification has been questioned by Cochran et al. (2002) who failed to detect this band in their high-resolution spectra of recent comets. H_2 has been detected in the UV with *FUSE* (Feldman et al. 2002), but it is presumably a daughter species coming from the dissociation of water and hydrocarbons.

[18] Ethylene glycol has recently been identified in archive radio spectra of comet Hale-Bopp (Crovisier et al. 2004, to be published). This is the most complex organic molecule firmly identified in a comet to date. [Note added in proof]

Concerning remote sensing investigations, the breakthrough performed in comets Hyakutake and Hale-Bopp has been, at best, repeated for some molecules in other bright comets which appeared since that time. For new progresses, we need sensitive new instruments, but also new bright comets. The real advantages of the new generation ground-based high-resolution infrared spectrometers (*IRTF/CSHELL*, *Keck/NIRSPEC* and *VLT/CRIRES* which will be soon available) have not yet been fully exploited due to line identification issues. The *ALMA*[19] radio telescope, to be completed in 2010, will achieve a gain in sensitivity of more than an order of magnitude over present instruments, when operating in the autocorrelation mode. The *Herschel Space Observatory* (to be launched in 2007) will give us access to a still shorter wavelength range, which cannot be explored from the ground. It will be adequate for probing light hydrides, but not for heavy molecules which have strong rotational lines at longer wavelengths.

Concerning space missions, the next step after *Stardust* and *Rosetta* should be the return of a cometary ice sample. An interesting technical challenge for the next generations.

5. Conclusion

There is now little doubt that *prebiotic* molecules are present in cometary ices. Evidences for more complex organic molecules are also present and indeed, we still have no idea of the limit in complexity of the cometary material.

There are also converging clues to the existence of a (semi-)refractory organic material composing a large fraction of the cometary grains. This material, of ill-defined composition, is likely to deliver lighter organic molecules through thermo-degradation.

Such organic matter probably does not survive giant cometary impacts. However, experimental simulations have shown that in specific conditions, amino acids could be delivered (Blank et al. 2001). Some of the simplest molecules could also be recomposed in the shock chemistry following impact.

On the other hand, cometary grains and small nucleus fragments could survive their delivery to Earth. They constitute part of the IDP's collected in the stratosphere, of the micrometeorites collected on the ground or in Antarctic ices. Indeed, they do contain complex heavy organic molecules. They have lost most of their volatiles, however.

[19] ALMA is a radio interferometer array of 64 $\times$ 12-m antennas to operate in the millimetre-submillimetre range.

Remote sensing observations will continue to assess the gross composition of cometary ices and its diversity from comet to comet. It will be limited by sensitivity and confusion, however, so that really complex trace species will escape to this technique.

In situ analyses could be more sensitive, but will be limited to a small number of objects. The analysis of the refractory organic cometary macro-molecules could be difficult because such material is expected to have an ill-characterized composition.

An expected return of cometary space exploration is to provide ground truth for discriminating cometary material in the extraterrestrial material available on Earth.

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