Molecular Physics, Vol. 00, No. 00, DD Month 200x, 1–15

Recent results and future prospects for the spectroscopy of comets*

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(*Revised version – May 23, 2006*)

The links between cometary science and molecular spectroscopy date back as far as ca 1860, with the beginnings of astronomical spectroscopy and astrophysics. In these days where the real nature of cometary material was quite unknown, cometary spectra were compared to laboratory spectra. By now, although the space exploration of comets is on the verge of performing the direct chemical analysis of cometary nuclei, this spectroscopic approach is still topical. Spectroscopic observations of comets allow us to determine the physical conditions (temperature, velocity field, density) of the cometary environment as well as the chemical composition of these bodies. This information is precious to understand how comets are working and how they interact with the solar environment. It gives us clues to the origin and first steps of the formation of the Solar System. It also allows us to evaluate the possible role played by comets in the origin of life, by bringing complex molecules to the early Earth. Observations of the exceptional comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) and other recent bright comets — taking advantage of the availability of efficient new instrumentation (both ground-based and space-based) in the radio, infrared and UV — revealed the molecular complexity of comets as well as their diversity. After the study of secondary products ("daughter molecules") which have spectroscopic signatures in the visible, we are now able to study molecules directly sublimated from cometary ices ("parent molecules"), using radio and infrared spectroscopy. More than two dozen such molecules are now known (not counting isotopic species). The last, most complex species identified to date is ethylene glycol, which has a remarkably high abundance relative to water. The most abundant compounds are now probably all known, but a wealth of minor components are still to be identified and studied. Many unidentified lines are present in cometary spectra, from radio wavelengths to the UV. Future progresses rely on the extensive study of cometary spectra, for which the use of comprehensive and reliable spectroscopic databases is crucial.

1 Introduction: Why study comets?

The study of comets is motivated in many ways:

- For the layman, comets are fascinating objects. They display unexpected, spectacular shows. For a long time, being quite unexplainable phenomena, they were associated with evil omens. They now have lost part – but not all – of their mystery, but the layman still wants to know what they are and how they work.
- For the physicist and the spectroscopist, comets are an exceptional laboratory where extreme conditions of temperature and density are met. This allows the investigators to observe unstable forms of matter, such as radicals and molecular ions, and specific phenomena, such as fluorescence, which are very difficult to study in Earth-based laboratory laboratories.
- For the astronomer, comets provide a key to understand the origin of the Solar System. They were formed in the early phases of the history of the Solar System, and were kept mostly intact because of their small gravity and low temperatures. Although they presumably formed at medium or far distances from the Sun, their orbits evolved into highly eccentric orbits, allowing a close inspection when they come close to the Earth and Sun.
- For the astrobiologist (aka bioastronomer), the study of Earth–comets relations is a must in the context of apparition and evolution of life, because the fall of comets on the early Earth was a possible source of

*Based on a review presented at the 19th Colloquium on High Resolution Molecular Spectroscopy, 12–16 September 2005, Salamanca, Spain

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Molecular Physics ISSN 0026-8976 print/ ISSN 1362-3028 online ©2005 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/002689700xxxxxxxxxx

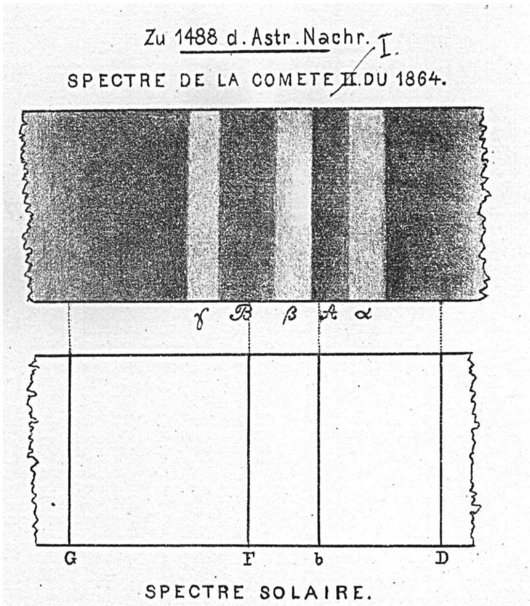

Figure 1. The drawing of the spectrum of comet C/1864 N1 (Tempel), observed visually by Donati [1]. The three emission bands α, β, γ were afterwards identified to fluorescence of the Swan bands of the C_2 radical. The solar spectrum is shown at the bottom to give the wavelength scale.

water and prebiotic molecules, and because comet-Earth collisions were — and still are — a potential danger for mankind and a possible cause of species extinction.

The present article is devoted to cometary molecules and their study by means of spectroscopy, keeping in mind all these motivations. The current state of molecular spectroscopy of comets is reviewed, in relation with the understanding of their chemical composition and physical properties. (The study of cometary dust is beyond the scope of this paper.)

2 Cometary spectroscopy in a historical perspective

The first reported spectroscopic observation of a comet was made visually in 1864 by Giovanni Donati in Florence, on a comet (C/1864 N1) just discovered by Wilhelm Tempel in Marseilles [1] (Fig. 1). Donati reported: "Le spectre de la comète ressemble aux spectres produits par les métaux; en effet les parties noires y sont plus larges que les parties lumineuses, et on pourrait dire que ces spectres se composent de trois raies claires telles que α, β et γ." ("The spectrum of the comet looks like spectra of metals; indeed, the black bands are wider than the bright bands, and one could say that these spectra consist of three bright lines such as α, β and γ.") This was the discovery of fluorescence emission by cometary molecules. These bands were identified to the Swan bands (now known to be due to the C_2 radical) four years latter by Huggins [2], still visually, in comet C/1868 L1 (Winnecke). Huggins used a clever device which allowed him to compare simultaneously the comet's spectrum and the spectrum of hydrocarbon vapours undergoing an electric discharge, thus establishing a direct link between observations at the telescope and measurements in the laboratory.

Last summer, on 4 July 2005, an active experiment was made on another comet discovered by Wilhelm Tempel in Marseilles in 1867: short-period comet 9P/Tempel 1 [3]. A 365-kg impactor hit the comet with a 11 km s^{-1} velocity. The event was observed by the *Deep Impact* spacecraft which released the impactor, as well as by most major Earth-based and space observatories, from radio wavelengths to X-rays [4].

In the lapse of time which separated these two pioneering observations of the two *Tempel* comets, considerable changes in the techniques of observation were achieved. As an example, Fig. 2 shows a portion of the visible spectrum of a moderately bright comet observed with modern techniques, to be compared with Donati's observation (Fig. 1). Still more spectacular are the opening to the radio, infrared and ultraviolet spectral domains, and the emergence of space astronomy and space exploration of the Solar

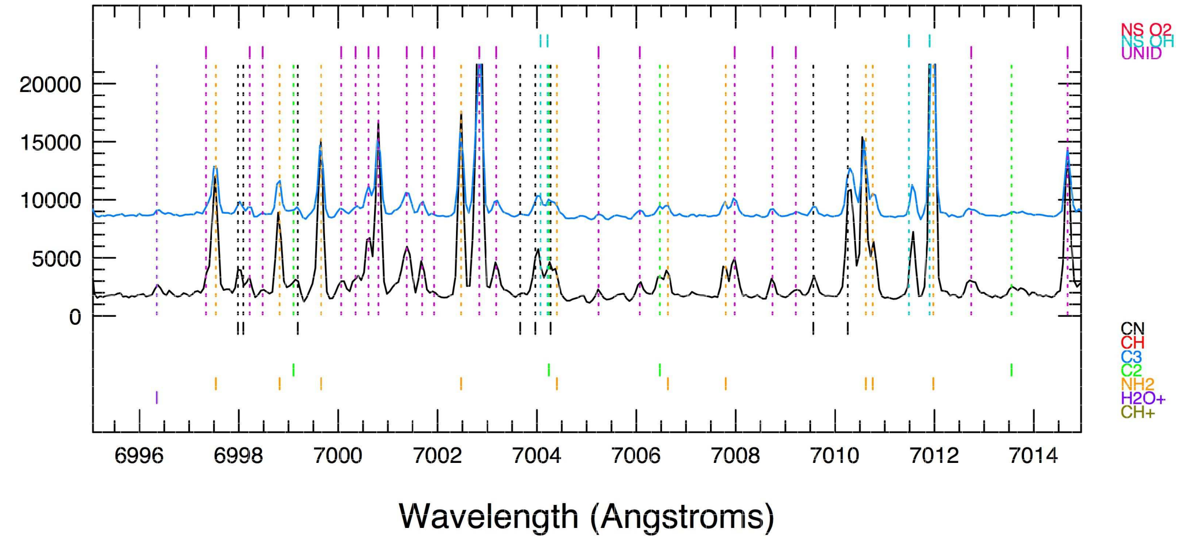

Figure 2. Excerpt of the high-resolution spectrum of comet 122P/de Vico in the visible. Lines of CN, C_2 and NH_2 are present, together with many unidentified features. (Adapted from [5].)

Table 1. Facts on typical comets.

Comet	period	nucleus size[a]	gas production[b]		dust production[c]
	[yr]	[km]	[10^{28} s^{-1}]	[kg s^{-1}]	[kg s^{-1}]
67P/Churyumov-Gerasimenko	6.6	4	1	300	400
21P/Giacobini-Zinner	6.6	2	5	1 500	400
1P/Halley	76	11	100	30 000	20 000
C/1995 O1 (Hale-Bopp)	2400	75	1 000	300 000	600 000

[a] Equivalent nucleus diameter.

[b] Water production rate by number of molecules and by mass at $r_h \approx 1$ AU.

[c] Dust production rate at $r_h \approx 1$ AU (the evaluation of cometary dust production in mass is highly model-dependent; we have assumed here that the dust production indicator $Af\rho = 1$ cm corresponds to 1 kg s^{-1}).

System (see illustrations in the following sections).

The early days of cometary spectroscopy, restricted to visible observations, were reviewed in a historical perspective in [6–10]. As will be detailed in the following sections, cometary spectroscopy has been revolutionized these last decades with the advent of large, sensitive telescopes, the opening to new spectral domains — radio, infrared, UV — using ground-based or space facilities, and last but not least, the possibility to make in situ investigations with space missions. For recent reviews on cometary molecules and their observation, see [11–20].

3 Physical conditions in comets

The atmosphere of an active comet is similar to a free molecular jet: ices sublimate at the nucleus surface, presumably at an equilibrium temperature $\approx$ 150–200 K; due to the very low gravity field of the comet, its atmosphere is not captive and expands. The expansion velocity rapidly becomes supersonic with $v_{\rm exp} \approx 0.5$–1 km s^{-1}. The expansion is first nearly adiabatic and the atmosphere cools down to very low temperatures ($T \approx 10$ K or less is observed in some cases). However, heating may occur through collisions with high-velocity photodissociation products; $T \approx 100$ K or more may be observed in the outer coma [21, 22].

Thus, physical conditions in a cometary atmosphere evolve progressively from a collisional region at thermal equilibrium in the inner coma to a large collision-free region with out-of-equilibrium processes farther from the nucleus.

Table 2. Typical conditions[a] in cometary atmospheres, interstellar clouds, and circumstellar envelopes.

		comet at 1 AU	diffuse cloud	dense cloud	hot core	circumstellar envelope
archetype object		1P/Halley		TMC 1	Orion IRc2	IRC+10216
size	[km]	$\approx 10^{6}$ [b]		$\approx 10^{13}$	$< 3 \times 10^{12}$	$\approx 10^{11}$
density	[particles cm^{-3}]	$10 - 10^{12}$	100	$10^{3} - 10^{7}$	$\approx 10^{7}$	$1 - 10^{12}$
temperature	[K]	10–100	≈ 100	10	≈ 200	10–2000
pressure	[mbar]	10^{-6} [c] – 10^{-17}	$\approx 10^{-16}$	10^{-11}–10^{-15}	$\approx 10^{-10}$	10^{-5}–10^{-18}
expansion vel.	[km s^{-1}]	1				10–20
H_2O lifetime	[s]	10^{5}	$\approx 10^{9}$			10^{9}

[a] These *typical conditions* are often subjective, ill-defined, or correspond to a broad range of values. The listed values must be considered as order-of-magnitude evaluations.

[b] Size of the molecular coma.

[c] Pressure close to the nucleus surface.

Comets are not all alike. Table 1 lists the properties of some typical comets: 67P/Churyumov-Gerasimenko is the target of the *Rosetta* mission; 21P/Giacobini-Zinner is a typical Jupiter-family comet, believed to have formed in the Kuiper belt, among trans-Neptunian objects, and to have evolved subsequently into a short-period comet; 1P/Halley is believed to have formed in the Jupiter–Uranus region, was expelled to the Oort cloud after gravitational interaction with the giant planets, and then evolved to a shorter orbital period; C/1995 O1 (Hale-Bopp) is a giant comet with an orbital evolution story similar to that of comet Halley.

Some basic parameters of the physical conditions of cometary atmospheres are listed in Table 2, together with the corresponding parameters for typical interstellar or circumstellar objects.

The low density of cometary atmospheres permits out-of-equilibrium emission processes to occur without being quenched by collisions. The main emission processes for cometary molecules are electronic and vibrational transitions following fluorescence excited by the Sun's radiation field [14, 15]. Emission rates (number of photons emitted per second by a given molecule, which is the so-called g-factor) are typically 10^{-4} s^{-1} for fundamental bands of vibration, 10^{-3} to 10^{-2} s^{-1} for electronic systems at 1 AU from the Sun. Unfortunately, the electronic systems of most of the stable molecules are in the UV where their excitation leads to photodissociation rather than to fluorescence (exceptions are CO, S_2 and H_2, for which UV fluorescence is observed in comets). Thus, all emission bands observed in the visible spectra of comets are due to secondary photolytic products — radicals or molecular ions. Another important emission process for cometary molecules (and atoms) is *prompt emission* (aka *chemical pumping*), when a photolytic product is created in an excited state; it is observed for CO (Cameron bands) produced from the photodissociation of CO_2, for the oxygen atom (forbidden lines) produced from the photodissociation of H_2O.

Rotational lines, in the radio spectral domain, are excited both radiatively as the final step of the fluorescence cascades, and thermally by collisions. In addition to neutral–neutral collisions, neutral–ion and electronic collisions must also be considered. A detailed modelling of the evolution of the rotational population distribution, as the molecules expand from the nucleus, is necessary and must take into account the balance between fluorescence excitation, collisions, and spontaneous decay. For abundant molecules with strong lines such as water, radiative trapping is an important process which must also be taken into account.

Chemistry in the coma is dominated by photolytic processes: degradation of *parent* species (molecules directly issued from the sublimation of nucleus ices) into *daughter* species (radicals, atoms, molecular ions). The low density and low temperature do not permit efficient two-body reactions. Exceptions are reactions with ions, created by photoionisation or by interaction with the solar wind, and reaction with *fast products*, essentially fast hydrogen created through photolysis; but the abundances of species created by such reactions are marginal compared to the abundances of the majority of molecules coming from ice sublimation and their decay products [24].

High-resolution molecular spectroscopy of comets is adequate to the investigation of the physical conditions in their atmospheres:

- The profiles of molecular lines are purely Doppler. Their observation at high resolution by radio tech-

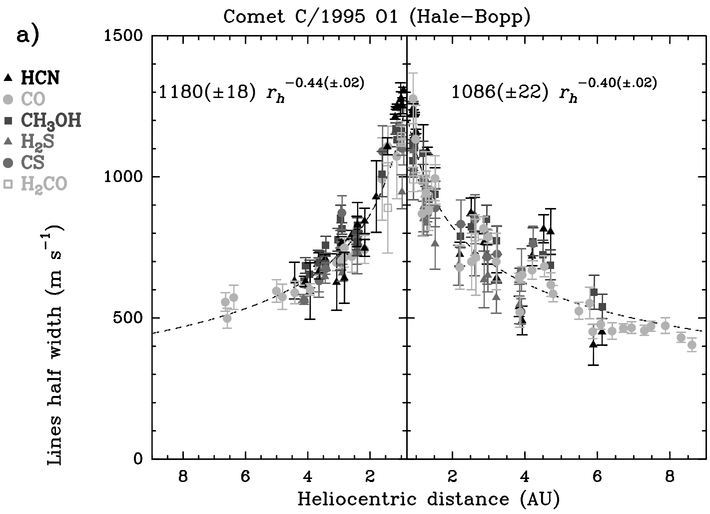

Figure 3. Expansion velocities observed in comet C/1995 O1 (Hale-Bopp). These velocities are inferred from the shapes of various radio lines. They are plotted as a function of heliocentric distance (left: pre-perihelion; right: post-perihelion). Fitted power laws are indicated. (From [23].)

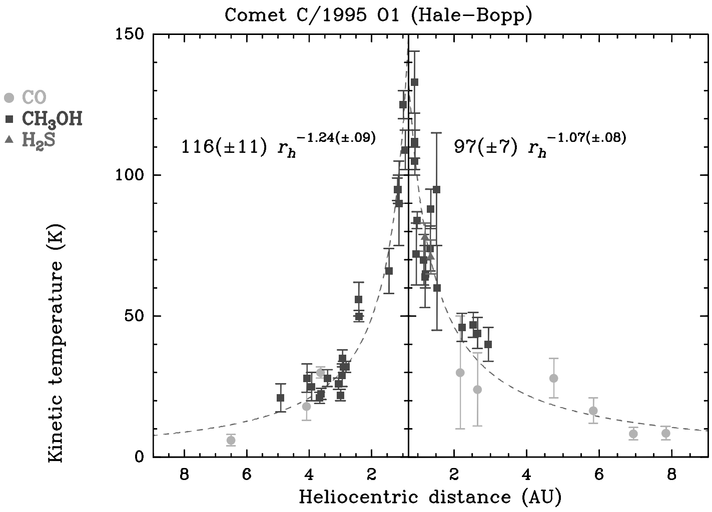

Figure 4. Temperatures observed in comet C/1995 O1 (Hale-Bopp) as a function of heliocentric distance (same presentation as in Fig. 3). The temperatures are inferred from the comparison of several radio line intensities of CO and CH_3OH. As for the velocities plotted in Fig. 3, they are averaged over the region sampled by the radio telescope beam, which is typically 10^3 to 10^4 km from the nucleus. The expansion velocity and the temperature of the atmosphere increase as the comet gets close to the Sun because of an increase of the photolytic heating. (From [23].)

niques permits to probe the kinematics of the cometary atmosphere, and to estimate its expansion velocity. Typical velocities of 0.5 to 1.5 km s^{-1} are observed [22, 23] (Fig. 3).

- The simultaneous observation of several rotational lines, or of several ro-vibrational lines of the same molecule allows us to determine the rotational population distribution, and therefore, of the rotational temperature. In the collisional region (inner coma), this temperature is close to the kinetic temperature. Typical temperatures from 10 to 100 K are observed [22, 23] (Fig. 4).

4 A census of cometary molecules

Molecular spectroscopy — at all possible wavelengths — is also adequate for a remote investigation of the chemical composition of cometary atmospheres and thus indirect probing of the composition of cometary ices. As we will see below, radio spectroscopy (which is very sensitive even for rare species [13, 16]) and mid-infrared spectroscopy (which is invaluable for the search for symmetric hydrocarbons [25]) proved to

Table 3. Molecules, radicals, ions and atoms observed in cometary comae[a].

Species	origin[b]	observations[c]	notes[d]	Species	origin[b]	observations[c]	notes[d]
H_2O	P	R, IR, MS		NH_3	P	R, IR, MS	
H_2O^+	S	V		HCN	P	R, IR, MS	
H_3O^+	S	R		HNC	?	R	
OH	S	R, IR, UV		CH_3CN	P	R, MS	
H	S	V, UV		HC_3N	P	R	
H_2	S	UV		HNCO	P	R	
O	S	V, UV		NH_2CHO	P	R	
O^+	S	UV		CN	S	R, IR, V	
CO	P,S	R, IR, UV, MS	E	NH	S	V	
CO_2	P	IR, MS		NH_2	S	IR, V	
CO^+	S	R, V, UV		N	S	UV	
CO_2^+	S	V		N_2^+	S	V	TBC
CH_4	P	IR		H_2S	P	R, MS	
C_2H_2	P	IR, MS		CS_2	P	V	TBC
C_2H_4	P	MS	TBC	CS	S	R, UV	
C_2H_6	P	IR, MS		SO_2	P	R	
C_4H_2	P	IR	TBC	SO	S	R	
CH	S	IR, V		OCS	P	R, IR	E
CH^+	S	V		H_2CS	P	R	TBC
CH_2	S	MS	TBC	NS	?	R	TBC
C	S	UV		S_2	?	UV	
C_2	S	IR, V, UV		S	S	UV	
C_3	S	V		Na	S	V	
H_2CO	P	R, IR	E	K	S	V	
CH_3OH	P	R, IR, MS		Ar	S	UV	TBC
HCOOH	P	R		metals[e]	S	V	
CH_3CHO	P	R	TBC				
$HCOOCH_3$	P	R	TBC				
$(CH_2OH)_2$	P	R					
HCO^+	S	R					

[a] The species detected by mass spectroscopy of comet 1P/Halley are taken from the compilation of [27, Table II]; also listed as "probably detected" were CS, OCS, CH_3CHO, C_3H_2 and C_2H_5CN [27, Table III].

[b] Origin: P – primary (or parent) molecule coming from nucleus ices or from an extended source such as dust; S – secondary molecule coming from photolysis of a primary molecule, or from chemical reactions within the coma.

[c] Observations : R – radio; IR – infrared; V – visible; UV – ultraviolet; MS – mass spectroscopy.

[d] Notes : TBC – the detection or identification of this species needs to be confirmed (e.g., a single line was observed in a single comet). E – this species is suspected to come (at least partly) from an extended source such as cometary dust.

[e] Various metal atoms were only observed in the sungrazing comet C/1965 S1 (Ikeya-Seki).

be the most efficient in the hunt for cometary molecules. Surface reflectance spectroscopy of cometary nuclei, which has been attempted on a limited number of objects either from space [3, 26] or from the ground, provided only little constraint on the composition of nucleus ices.

Our current knowledge of the chemical composition of cometary ices and of the gas-phase species of cometary atmospheres is summarized in Table 3 and Fig. 5. The most complete knowledge of the chemical composition of a comet was obtained for C/1995 O1 (Hale-Bopp) and many minor species were only observed in that comet (for a list of molecular abundances observed in comet Hale-Bopp and other bright comets, see [14, Table 1]). In situ mass spectroscopy was only performed for comet 1P/Halley and its results must be taken with a grain of salt, since they depend upon ion–neutral chemical modelling and are subject to instrumental mass ambiguity.

For a census of the elemental composition of comets, cometary dust must be also taken into account. Although no precise evaluation is available, this elemental composition is grossly consistent with that of the Sun, except for the most volatile elements (hydrogen, helium, noble gases) which are depleted.

4.1 *Detections and upper limits*

The most abundant compounds are now probably all known, but a wealth of minor components are still to be identified and studied. Significant upper limits have been obtained for many species from the analysis of

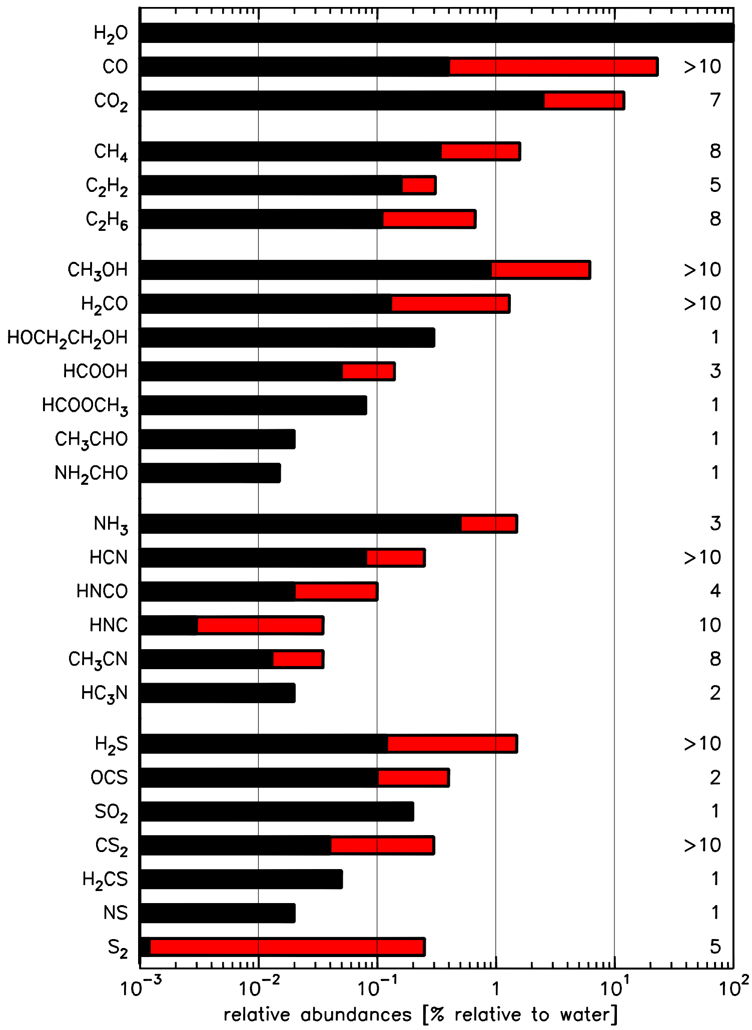

Figure 5. Relative production rates of cometary volatiles and their comet-to-comet variations. These rates are believed to trace the relative abundances in cometary ices. The grey part of each bar indicates the range of variation from comet to comet. On the right, the number of comets in which the species was detected is indicated. CO_2 data include direct infrared measurements as well as indirect measurements from CO prompt emission in the UV. CS_2 data include indirect determinations from UV and radio observations of the CS radical. Some species (e.g., H_2CO) are known to come (in part) from extended sources, not directly from the nucleus ices. The origins of NS and S_2 are ill-understood. (Updated from [14].)

radio spectra [16]. Others are potentially present in observed spectra, pending the availability of suitable molecular databases.

On the other hand, existing infrared cometary spectra have not yet been fully exploited.

4.2 *A case study: ethylene glycol*

An edifying case is the identification of ethylene glycol in comet Hale-Bopp. Some radio lines were detected in the spectrum of C/1995 O1 (Hale-Bopp), but could not be identified at the time of the observations [28]. Using a new theory of ethylene glycol $(CH_2OH)_2$ [29], this molecule was searched for and identified in the Galactic Centre [30]. As soon as the molecular data were posted in the Cologne Database for Molecular Spectroscopy (CDMS, [31]), we were able to identify this molecule from our archive spectra of comet Hale-Bopp [32]. One of the identification spectra is shown in Fig. 6.

The identification of ethylene glycol in the comet appears to be easier and more reliable than its iden-

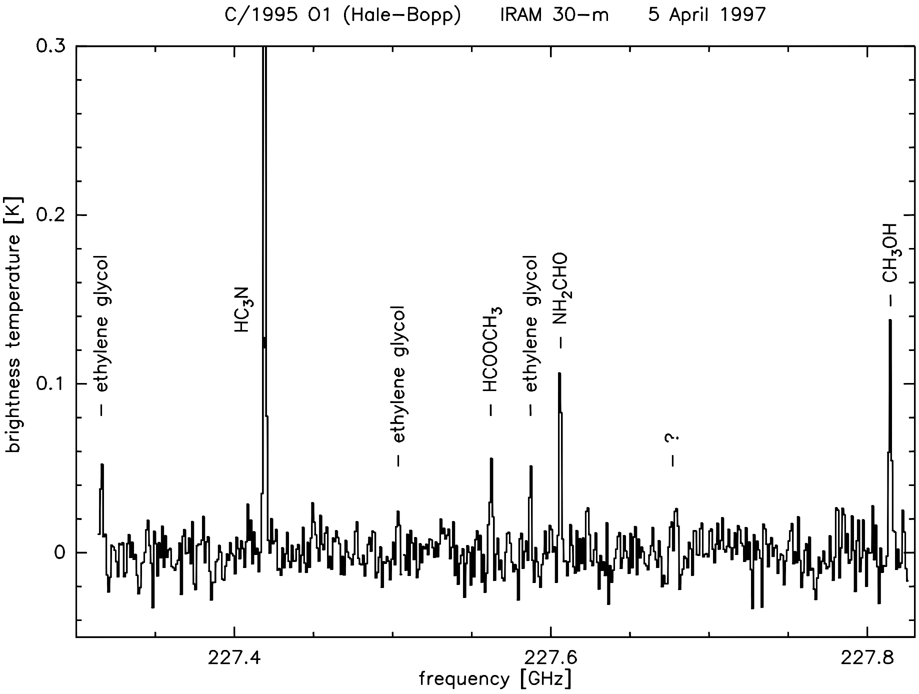

Figure 6. Detection of the radio lines of ethylene glycol and other complex organic species in C/1995 O1 (Hale-Bopp) with the *IRAM* 30-m telescope. (From [32].)

tification in the Galactic Centre. The cometary lines are narrower than the galactic lines (≈ 2 km s^{-1}, compared to ≈ 30 km s^{-1}) due to the different kinematics in these objects. Spectral confusion complicates the line identifications in the Galactic Centre radio spectrum which shows a forest of lines, most of them being blended.

4.3 *Molecules in homologous series*

As could be expected, the abundance of molecules decreases when their complexity increases. This is indeed observed for molecules in homologous series: saturated hydrocarbons (CH_4 = 1.5%, C_2H_6 = 0.6%), aldehydes (H_2CO = 1.1 %, CH_3CHO = 0.02%) and cyanopolyynes (HCN = 0.25%, HC_3N = 0.02%, HC_5N $<$ 0.003%) [16, 18, 25].

But surprisingly, the abundance of ethylene glycol is comparatively large: 0.25%, making it the third *CHO* molecule after methanol and formaldehyde. This dialcohol is even more abundant than ethanol ($<$ 0.10%) [16, 32].

4.4 *Evolution with heliocentric distances*

The evolution with heliocentric distance of the production rates of various molecules provides us with a clue to their sublimation mechanisms. Such a study could be performed on comet C/1995 O1 (Hale-Bopp); the activity of this giant comet could be followed up to considerable distances from the Sun [23]. At $r_h \approx$ 14 AU, CO could still be observed through its J(2–1) radio line.

All molecules do not behave in the same way, depending upon their volatility. The sublimation of water, which is the motor of cometary activity close to the Sun, is inefficient farther than ≈ 4 AU. The activity of distant comets is governed by the sublimation of *hypervolatiles*: mainly CO, but also CH_4 and perhaps N_2 if this molecule is present in cometary ices. We have to take this phenomenon into account when we try to deduce the relative molecular abundances in cometary ices from the abundances of the same molecules observed in the cometary atmosphere.

4.5 *Relations with interstellar molecules*

Basically, the same molecules are found in cometary atmospheres and in interstellar clouds. Two extreme hypotheses have been proposed: (i) cometary material is made of unprocessed interstellar material; (ii) cometary material underwent chemical processes in the primitive Solar Nebula in such a way that it has totally lost any chemical memory of the interstellar material from which it originates. The truth is probably between these two hypotheses. We must also have in mind that chemical processes in the primitive Solar Nebula could be very similar to those which occurred in interstellar clouds. This topic is discussed in [13, 33–35].

4.6 *Unidentified lines*

Many of the lines observed in cometary spectra — at all wavelengths — are still unidentified, showing that the work of interpretation which began in the XIXth century on the first cometary spectra is far from being over.

The best documented case is in the visible. For example, in the high-resolution spectrum of comet 122P/de Vico, 12 219 lines were identified (principally to CN, CH, C_2, C_3, NH_2, CH^+, CO^+, H_2O^+), but no less than 4 219 unidentified lines were reported [5] (Fig. 2). Indeed, a major fraction of them could be attributed to NH_2, from available data on this radical (Michel Vervloet, *personal communication*). H_2O^+ [36] and other molecular ions and radicals are plausible candidates for the identification of the others. CS_2 has also been proposed for some of the lines in the blue region [37].

In the UV, a breakthrough was recently made with the *FUSE* (*Far Ultraviolet Spectroscopic Explorer*) observations from space [15, 38]. Besides detections of lines from CO and H_2 (H_2 is indeed coming from photodegradation of water and other parent molecules rather than from nucleus ices), *FUSE* spotted several unidentified lines, likely due to atoms and ions [39].

In the infrared, low-resolution spectra have revealed 3.2 to 3.6 μm emission features that are still ill-understood [40]. *CHO* molecules and hydrocarbons (including PAHs) are obvious candidates for their identifications. Methanol, which is well studied at radio wavelengths, is certainly an important contributor, but we are still awaiting for a detailed theory of the infrared emission of this molecule to evaluate precisely its contribution. High-resolution spectra allowed us to identify several molecules in this spectral domain (Fig. 5, Table 3). But they also revealed many unidentified lines. Some of them could be due to radicals rather than simple stable molecules. The full exploitation of the existing high-resolution infrared spectra of comets is not yet done, and no comprehensive list of unidentified features is available for this spectral domain.

At radio wavelengths, some unidentified lines are still present, but with limited signal-to-noise ratios [16]. The successful identification of ethylene glycol to similar lines (see above) is a strong encouragement to proceed further with the identification of these lines.

There is an obvious need for extensive molecular databases and modelling.

5 Cometary water

Cometary water is an ubiquitous, but elusive cometary species. It is almost impossible to observe from the ground due its presence in the Earth's atmosphere.

Cometary water was first detected in the infrared from air-borne observations of comet Halley in 1985 [42]. From the ground, it could be observed through lines of its hot vibrational bands near 2 and 4.7 μm [43]; such observations are now conducted at high spectral resolution with large telescopes such as the *IRTF* or the Keck telescope (where the *NIRSPEC* instrument has a spectral resolution $\approx$ 25 000) [25, 44]. From space, the water infrared spectrum around 3.7 and 6 μm as well as rotational lines in the far-infrared were investigated with the *Infrared Space Observatory* (*ISO*) [45–47].

In situ observations of water in the infrared were first made by *VEGA/IKS* on comet 1P/Halley and recently by *Deep Impact* on 9P/Tempel 1 [3, 48] (Fig. 8). In the future, similar observations will be conducted more extensively on comet 67P/Churyumov-Gerasimenko at a higher resolution by the *VIRTIS*

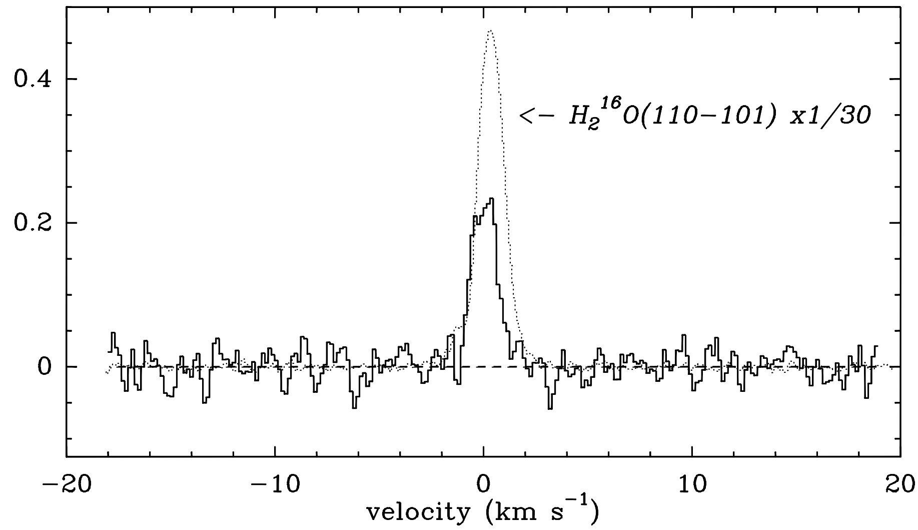

Figure 7. The 1_{10}–1_{01} lines of $H_2^{16}O$ and $H_2^{18}O$ near 550 GHz observed in comet C/2004 Q2 (Machholz) in January 2005 with the *Odin* satellite. The line frequencies have been converted into Doppler velocities in the comet frame of rest. Note the difference in the line shapes, which may be attributed to the large opacity of the $H_2^{16}O$ line. (From [41].)

instrument aboard *Rosetta* [49].

At radio wavelengths cometary water is also impossible to observe from the ground, except for the HDO isotopic species which was observed — difficultly and in only two comets — with the *CSO* (*Caltech Submillimeter Observatory*), *JCMT* (*James Clerk Maxwell Telescope*) and *IRAM* (*Institut de Radioastronomie Millimétrique*) telescopes, and which will be a goal for the future *ALMA* (*Atacama Large Millimetre Array*) facility. From space, the 1_{10}–1_{01} line of water at 557 GHz was extensively observed in about fifteen comets with the *SWAS* (*Submillimeter Wave Astronomy Satellite*) and *Odin* small telescopes [41, 50, 51] (Fig. 7). In the future, this line (as well as other submillimetric lines) will be an ideal target for the *Herschel Space Observatory* [52]. The *MIRO* instrument aboard *Rosetta* will also investigate in situ this line and those of other water isotopic species in comet 67P/Churyumov-Gerasimenko [53].

6 Isotopic ratios

Isotopic ratios, which have been investigated spectroscopically for D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$, $^{15}N/^{14}N$ and $^{34}S/^{32}S$, will not be discussed here. See [54] for a general review and [14, 19, 20] for recent results.

7 Ortho-to-para ratios and spin temperatures

For molecules such as H_2O, NH_3, CH_4 which exist in different spin species (*ortho–para*, *A–E*...), spin transitions are forbidden, so that spin temperatures could be preserved for a long time. The ortho-to-para ratios (OPR) and spin temperatures observed now for cometary water or for other species might thus be primordial [21, 55].

First determinations of the water OPR were made from air-borne infrared observations of comets 1P/Halley and C/1986 P1 (Wilson) [33]. Then accurate measurements were obtained with *ISO* on comets C/1995 O1 (Hale-Bopp) and 103P/Hartley 2 [45, 46]. Further results on water were obtained by observing vibrational hot bands of water from the ground on bright comets [56].

These results were extended to ammonia. The OPR of NH_3 itself cannot (yet) be directly observed, but can be derived from the OPR of NH_2 determined from its visible spectrum [57]. The spin temperature of methane can also be determined from the E, A, F spin species relative populations measured from its infrared spectrum.

All these results were recently reviewed in [58] (see also [56, 59] for last results on methane and water spin temperatures). These results are quite puzzling: the observed spin temperatures are remarkably close to 30 K, whatever the molecule, the heliocentric distance of the comet or its dynamical history.

What is the signification of this *universal* temperature? Is it really primordial — as was first believed —, tracing the temperature of formation (or condensation) of the molecules, which would thus be the same for all molecules and all comets? Or is it the consequence of a local re-equilibration, at a temperature which would also be the same for all comets? It seems that all the proposed explanations cannot fully explain the observations. Laboratory simulations of comet analogue material in cometary conditions would be helpful to investigate the time scales for equilibration of the spin populations, and their behaviour during phase transitions.

8 Problems of cometary chemistry

There are still many pending problems related to cometary molecules. Among the various molecules now observed in cometary atmospheres, several have unknown filiation: we do not know for certain whether they are coming directly from nucleus ices, from photodegradation of parent molecules, from two-body chemical reactions within the coma, or from degradation of large-size molecules in cometary grains. This is the case for the S_2 molecule and the NS radical; they are unlikely to be present in cometary ices, but no plausible other sources could be found. The parents for the C_3 radical are still to be found: HC_3N is not abundant enough, and propyne (CH_3CCH) is not detected with a significant upper limit.

Although CN is one of the best studied cometary radicals, its origin is not fully elucidated [60]. Indeed, HCN should be one of its major parents, but evaluations of production rates show that there may be significant additional sources. Isotopic measurements have shown that the $C^{15}N/C^{14}N$ and $HC^{15}N/HC^{14}N$ ratios differ by a factor of two, also suggesting an additional source [61]. HNC, an unstable isomeric form of HCN, is also observed in comets. The observed HNC/HCN ratio, which may be as large as 0.2, varies from comet to comet and increases when the heliocentric distance decreases. The origin of cometary HNC is unclear since models of cometary chemistry rule out a HCN $\rightarrow$ HNC conversion in the coma, at least in weak comets. The degradation of cyanopolyyne polymers has been invoked.

The existence and nature of extended sources of molecules in cometary comae is subject to debates. Cometary formaldehyde is now well known to come mainly from an extended source rather than from the nucleus; the thermal degradation of polymers such as polyoxymethylene has been proposed for its origin [62]. The idea of an extended source of carbon monoxide comes from in situ exploration of comet Halley and from infrared observations of comet Hale-Bopp, but its existence is controversial [14, 63] and there is no definite clue to its nature. This is an important issue, since CO is a major cometary volatile molecule, mainly responsible for the activity of distant comets.

What is the true nature of these extended sources? Complex molecules, icy grains, organic grains, chemistry in the coma? The answer will possibly come from in situ analyses of cometary material.

9 The space exploration of comets

9.1 *The first missions*

The space exploration of comets at a close distance, with imaging and spectrocopic instrumentation, was inaugurated with the *VEGA 1*, *VEGA 2* and *Giotto* flybys of comet P/Halley in March 1986 (Fig. 8). Only short-time observations could be made due to the high encounter velocities (≈ 70 km s^{-1}).

The following missions, *Deep Space 1* towards 81P/Borrelly and *Stardust* towards 19P/Wild 2, had not the possibility to make spectroscopic investigations of the coma. *Stardust* succeeded in bringing back (on 15 January 2006) samples of cometary dust particles collected in the coma [64]; unfortunately cometary ices were preserved, but refractory organic matter might still be present.

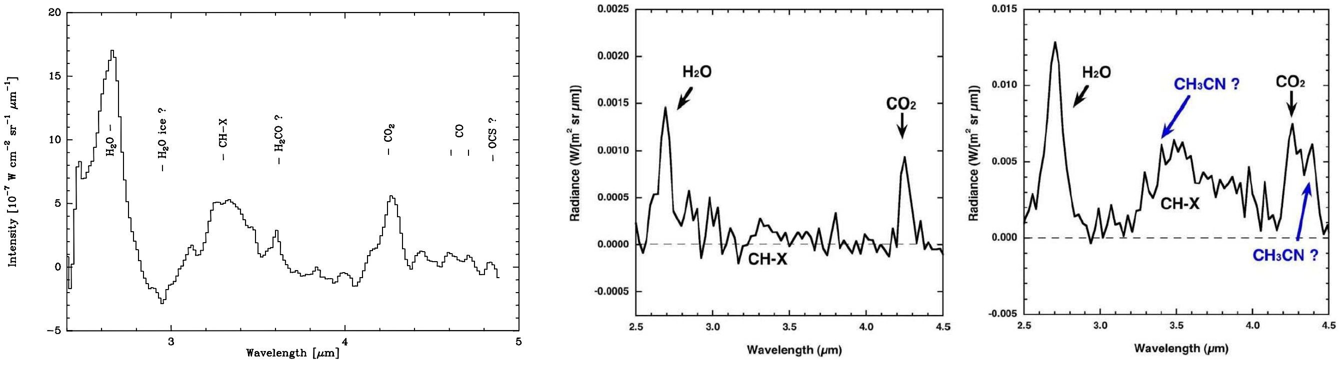

Figure 8. The 2.5–5 μm infrared spectrum of comets from space exploration, showing the main cometary volatiles. Left: 1P/Halley observed by *VEGA/IKS* on 6 Mars 1986 at ≈ 50 000 km from the nucleus [48]. Right: two limb-sounding spectra of 9P/Tempel 1 observed by *Deep Impact* taken 4 min before and 10 min after the impact (from left to right) on 4 July 2005, at respectively ≈ 11 000 and 2 500 km from the nucleus [3].

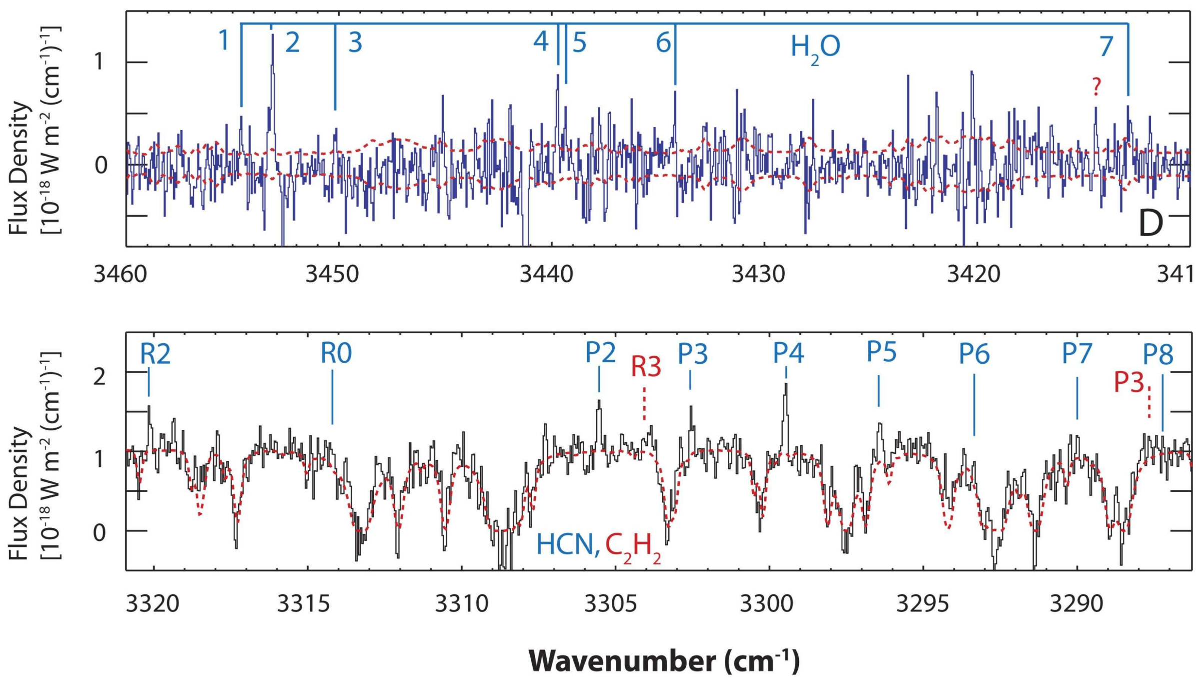

Figure 9. A portion of the infrared spectrum of comet 9P/Tempel 1 observed with the Keck telescope just after the *Deep Impact* event, showing ro-vibrational lines of water, acetylene and hydrogen cyanide. (From [65].)

9.2 *Deep Impact*

The idea of the *Deep Impact* mission — the first active experiment on a comet — was to excavate matter from ≈ 10–30 m under the surface of the nucleus, to check whether the material released in the coma by sublimation is representative of inner nuclear material. For this, a 365 kg impactor hit the comet with a 11 km s^{-1} velocity [66].

The first reports confirm the full success of the experiment [3, 4, 65, 67] (Figs 8 and 9). At a distance, the Earth-based observations do not easily separate the matter released by the impact from that due to the quiescent activity of the comet, so that an elaborate analysis is needed for interpretation. The spectra observed from the spacecraft itself show a huge increase of the signal after the impact (Fig. 8). But the molecular bands appear to be optically thick, so that sophisticated radiative transfer modelling is required. It is thus still premature to draw definitive conclusions on the results.

9.3 *Rosetta*

ESA's spacecraft *Rosetta*, launched on 2 March 2004, will encounter comet 67P/Churyumov-Gerasimenko and study it at a close distance in 2014–2015 [68]. A small robotic probe (*Philae*) will land on the nucleus for direct analyses.

The *Rosetta* orbiter will study 67P/Churyumov-Gerasimenko and its environment over a large range of heliocentric distances, allowing us to study the evolution of its activity. Mentioning only instruments relevant to molecular studies, the orbiter is equipped with mass spectrometers (*COSIMA* and *ROSINA*, with a resolution able to resolve most mass ambiguities) and with spectrometers at spectral wavelengths from radio to UV: *MIRO* [53] will observe at high spectral resolution the lines of water, water isotopomers and several other dedicated species; *VIRTIS* [49] will investigate the 2–5 μm spectrum of the comet with a resolution $\approx$ 2000; *ALICE* [69] will observe radicals, ions and atoms in the coma in the UV (70–205 nm with a resolution $\approx$ 200). The lander *Philae* is equipped with an X-ray spectrometer (*APXS*), mass spectrometers and a gas chromatograph (*PTOLEMY* and *COSAC*).

10 Conclusion

The historical synergy between spectroscopy and cometary science is still alive. Spectroscopy has proved to be a major tool for remote sensing studies of comets. In turn, comets are still a convenient laboratory for studying molecules in extreme physical conditions.

Recent studies, taking benefit of new technology and/or exceptional targets, gave answers to some old questions, but also brought up new questions:

- We probably now know what are the main constituents of cometary ices. Which cometary molecules are still to be identified?
- Molecules as complex as ethylene glycol have been identified in cometary atmospheres. What is the limit of the complexity of cometary molecules?
- Several molecules of biological relevance have been identified in comets. However, how they could survive in collisions of comets with the Earth is a debated issue [70, 71]. What was the role of comets in the chemistry of early Earth and in the apparition of life?
- Large chemical differences are observed from comet to comet. What is the link between this chemical diversity and the origin and evolution of comets?
- Beside in situ exploration, remote sensing spectroscopy is still useful to the study of comets, because the comet population has to be studied as a whole, whereas space exploration is limited to a few objects.
- 150 years after, the systematic study of cometary spectra is still topical. Extensive molecular databases are crucial for the analysis of complex cometary spectra.
- *Rosetta* will perform an in-depth in situ analysis of cometary material. The next step will be to return to Earth a real sample of cometary nucleus.

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