Lessons of Comet Hale-Bopp for Coma Chemistry: Observations and Theory.

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Abstract. Many new cometary molecules – both parents and daughters – were detected in the exceptionally productive comet C/1995 O1 (Hale-Bopp). The space distribution of several of these species could be investigated from radio interferometry or from long-slit spectroscopy in the infrared. The distinction between parent species – directly sublimated from nucleus ices – and secondary species – resulting from chemical processing in the coma or produced by a secondary source – is not always clear.

It is important to assess whether or not observed minor species ($HCOOCH_3$, HCOOH...) could be synthesized by chemical reactions favoured by the high density of the coma of comet Hale-Bopp. Chemical modelling by Rodgers & Charnley suggests that this is not the case. CO and H_2CO are abundant cometary species which partly come from distributed sources. The nature of these sources is still a mystery. A special case, now well documented, is that of HNC, for which the abundance evolution with heliocentric distance could be observed in comet Hale-Bopp and which was observed in several much less productive comets.

Keywords: Astrochemistry, Comet C/1995 O1 (Hale-Bopp), Comets, Molecular processes, Molecules

1. Introduction

One of the fundamental problems of cometary science is to establish the chemical constitution and physical nature of cometary material. The conjunction of the apparition of the great comet C/1995 O1 (Hale-Bopp), among one of the brightest comets of the 20th century, with the emergence of new observational facilities, allowed us to make unprecedented progress on this topic. Together with those performed one year before on comet C/1996 B2 (Hyakutake), the observations of comet Hale-Bopp led up to almost triple the number of known molecules directly produced by nucleus ices. These results strengthened the similarity between cometary and interstellar ices, which was one of the strong ideas brought up by Mayo Greenberg (1982, 1998).

Our purpose here is to review what we learned from the observations of comet Hale-Bopp on the chemistry of the coma (excluding refractory dust). We will emphasize the work done since the *First International*

Conference on Comet Hale-Bopp held in 1998 as well as significant progresses obtained on other comets since that time.

Section 2 draws up the inventory of cometary molecules, with their relative abundances. Section 3 deals with the observations of extended sources of cometary molecules. Section 4 is on the chemical models required for the interpretation of molecular observations: could we explain the presence of some of the observed minor species by chemical synthesis in the coma, and do we understand the production of molecules from grains? Section 5 puts forward some other specific issues related to molecular processes. Section 6 summarizes the pending questions that should trigger future work.

2. The inventory of cometary molecules

2.1. The inventory at the time of the last conference

Due to its exceptional brightness, C/1995 O1 (Hale-Bopp) is up to now the comet which permitted the observation of the largest number of molecular species. All atoms, molecules, radicals and ions ever observed in comets were observed in comet Hale-Bopp, with the exception of N_2^+ (see below), S_2 (only observed in comets C/1983 H1 (IRAS-Araki-Alcock) and C/1996 B2 (Hyakutake)) when they passed close to the Earth), H_2 (see below), and the metallic atoms only observed in the Sun-grazing comet C/1965 S1 (Ikeya-Seki).

Tables I and II summarize our knowledge of molecular abundances for comet Hale-Bopp. These are mainly taken from Bockelée-Morvan et al. (2000) and Crovisier et al., *in preparation*.

2.2. Recent results

1. Acetaldehyde (CH_3CHO). The presence of CH_3CHO was suspected from marginal features observed in comet Hale-Bopp with the *IRAM* 30-m telescope. It was confirmed afterwards by inspecting an archive spectrum obtained with the *IRAM* interferometer (Crovisier et al., *in preparation*).

2. The NS radical. NS was discovered in *JCMT* archive spectra of comet Hale-Bopp by Irvine et al. (2000). Its production rate is evaluated to be at least 0.02 % that of water. No simple parent molecule could be found for this radical (HNCS, HNSO and NH_4SH have been proposed).

Table I. Relative production rates of molecules observed in comet C/1995 O1 (Hale-Bopp) at $r_h \approx 1$ AU.

Molecule	[a]	$[X]/[H_2O]$	remark
H_2O	IR	100	
HDO	Radio	0.06	
CO	Radio IR UV	23	extended[b]
CO_2	IR	20[c]	
CH_4	IR	0.6	
C_2H_2	IR	0.2	
C_2H_6	IR	0.6	
CH_3OH	Radio IR	2.4	
H_2CO	Radio IR	1.1	extended[d]
HCOOH	Radio	0.09	
CH_3CHO	Radio	0.02	
$HCOOCH_3$	Radio	0.08	
NH_3	Radio IR	0.7	
HCN	Radio IR	0.25	
DCN	Radio	6×10^{-4}	
HNCO	Radio	0.10	
HNC	Radio	0.04	extended
CH_3CN	Radio	0.02	
HC_3N	Radio	0.02	
NH_2CHO	Radio	0.015	
H_2S	Radio	1.5	
OCS	Radio IR	0.4	extended
SO	Radio	0.3	extended [e]
CS	Radio UV	0.2	[e] (from CS_2)
SO_2	Radio	0.2	
H_2CS	Radio	0.02	
NS	Radio	0.02	[e]

Adapted from Bockelée-Morvan et al. (2000) with updates from Crovisier et al. *in preparation* (CH_3CHO), Meier et al. (1998a) (DCN), Meier et al. (1998b) (HDO), Dello Russo et al. (2001) (hydrocarbons), Irvine et al. (2000) (NS).

[a] technique of observation;
[b] abundance given for *nuclear + extended* source;
[c] measured at $r_h = 2.9$ AU;
[d] abundance given for *extended* source;
[e] probably a daughter species.

Table II. Molecular upper limits in comet Hale-Bopp from radio observations. (From Crovisier et al. *in preparation*.)

molecule	$[X]/[H_2O]$	molecule	$[X]/[H_2O]$
H_2O	100	NS	< 0.01
H_2O_2	< 0.03	H_2CS	< 0.04
CH_3CCH	< 0.045	NaOH	< 0.0003
CH_2CO	< 0.032	NaCl	< 0.0008
C_2H_5OH	< 0.05	HDCO	< 0.05
CH_3OCH_3	< 0.45	CH_3OD	< 0.07
glycine I	< 0.5	CH_2DOH	< 0.01
HC_5N	< 0.003	NH_2D	< 0.08
CH_2NH	< 0.032	HDS	< 0.3

All upper limits are given at the 3–σ level.

3. Supervolatiles: N_2 and argon

   The presence of very volatile species, such as N_2 and noble gases, in cometary ices would present a stringent clue to the temperature at which cometary material formed.

   The presence of N_2 is founded historically on the identification of a N_2^+ band in the spectra of comets observed photographically in the early 20th century. However, N_2^+ could not be identified in high S/N, high resolution spectra of comet Hale-Bopp, nor in similar spectra of 122P/de Vico (Cochran et al. 2000). The identification of N_2^+ in other comets relies on spectra with limited resolution, in a region where blends with CO^+, CO_2^+, CH and CH^+ bands are possible. The real presence of N_2^+, and therefore of N_2 in comets, is thus controversial.

   The identification of argon in comet Hale-Bopp was claimed by Stern et al. (2000) from the observation of its multiplet at 105 nm in comet Hale-Bopp with *EUVS*. However, due to the limited S/N and to the presence of unexplained features near the argon line, this detection would need confirmation. A search of the same line with *FUSE* in comet C/2001 A2 (LINEAR) was negative, indicating a [Ar]/[O] ratio strongly depleted with respect to solar abundances (Feldman et al. 2001).

4. H_2 molecule. The *FUSE* satellite opened a new spectral domain for cometary observations. New electronic systems of CO (*C*–*X* and *B*–*X* at 109 and 115 nm) were observed in comets C/1999 T1

(McNaught-Hartley) and C/2001 A2 (LINEAR). The H_2 molecule was observed, for the first time in a comet, through lines of its B–X (Lyman) system around 110 nm in C/2001 A2 (LINEAR) (Feldman et al. 2001). Cometary H_2 comes mainly from the photodissociation of water, but also from hydrocarbons. Due to its long lifetime, it is expected to be the most abundant molecular species in the coma (in terms of total number of molecules).

2.3. Unidentified species

The presence of many unidentified lines at all wavelengths in cometary spectra shows the need for laboratory and theoretical work on the spectroscopy of radicals, ions, unstable and complex molecules.

1. Radio

   Not so many unidentified lines are noted in the radio domain (Crovisier et al. *in preparation*), but only a small fraction of this spectral domain has yet been explored.

2. Infrared

   Cometary emissions in the 3.2–3.5 μm region, first noted in 1P/Halley, are still not understood. They are presumably due to hydrocarbons (including PAH's) and CHO species. Methanol is certainly contributing, but a precise evaluation of this contribution is still awaiting a detailed theory of the CH_3OH infrared spectrum.

   Unidentified discrete lines were noted in the *IRTF/CSHELL* spectra of comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) (Brooke et al. 1996; Magee-Sauer et al. 1998). Many new lines and bands were recently observed in the high-resolution *NIRSPEC* spectra, especially in comets C/1999 H1 (Lee) and C/1999 S4 (LINEAR) (Mumma et al. 2001). Some of them could be identified as OH and CH_3OH lines, but a large number remain unidentified. Their study, which probably requires further laboratory spectroscopic work, could lead to a bonanza of new cometary molecules.

3. Visible

   The presence of unidentified lines in visible cometary spectra is a problem as old as astronomical spectroscopy itself.

   All the data from comet Hale-Bopp have not yet been been published and are far from being fully exploited (see Zhang et al. 2001 however). Cochran & Cochran (2002) have just published their monumental atlas of the visible spectrum of 122P/de Vico, from which they list 12 219 identified, and 4 055 unidentified lines.

4. UV

   Several unidentified lines were recently observed with FUSE (Feldman et al. 2001). They could be due to atoms and ions, but molecules cannot be excluded.

5. X-ray emission

   The nature of the X-ray emission observed in comet Hale-Bopp and several other comets was a mystery at the time of the *First International Conference on Comet Hale-Bopp*. It has now been identified to line emission of multi-charge ions created by solar wind charge transfer, from analyses of the X-ray spectra of C/1996 B2 (Hyakutake) (Krasnopolsky & Mumma 2001) and C/1999 S4 (LINEAR) (Lisse et al. 2001), as was suggested first by Cravens (1997).

3. Nuclear versus extended sources: Observational clues

One of the highlights of the space investigation of comet 1P/Halley was that some molecules present in the coma were not originating from the nucleus, but released or produced from a distributed source. The strongest pieces of evidence were for CO (Eberhardt et al., 1987) and H_2CO (Meier et al., 1993). Their spatial distributions measured *in situ* by the Giotto mass spectrometer do not match those expected for a parent molecule and require distributed sources of scale lengths $\approx$ 5000 km (H_2CO) to 10 000 km (CO) contributing to half the total CO production and most of the H_2CO production of the comet. Coarse mapping of H_2CO millimetre lines in comets C/1989 X1 (Austin), C/1990 K1 (Levy) and C/1996 B2 (Hyakutake) confirmed the extended nature of H_2CO production in cometary comae (Colom et al., 1992; Biver et al., 1999b). The presence of distributed sources of radicals, other than their gas parents, was suggested for explaining CN, C_2 and C_3 gas jets seen in P/Halley (see the review of Festou, 1999).

Table III summarizes observational evidence for extended sources in comet Hale-Bopp. Observational pieces of evidence are of different kinds. The most direct ones are from the study of the spatial distribution of molecular emissions. Inversion from intensity to density profiles requires appropriate modelling of emission processes along the field of view, including opacity effects (DiSanti et al., 2001). Infrared spectroscopy using long slit (typically 30", with seeing-limited angular resolution) provided information concerning H_2O, HCN, CO, OCS and C_2H_6 (Dello Russo et al., 1998, 2000, 2001; DiSanti et al., 1999, 2001;

Table III. Evidence for extended sources in comet C/1995 O1 (Hale-Bopp)

Method	CO	H_2CO	HNC	OCS	SO	other species
Spatial distribution :						
long-slit spectroscopy	yes			yes		
interferometry	?	yes	?		yes	
Heliocentric evolution	?	yes	yes	yes		CS
Line shapes at large r_h	?	yes				CH_3OH, H_2O (from OH)
Others						CN, C_2, OH ...

Note : question marks mean that either data are available and still under study, or that the evidence is questionable.

Magee-Sauer et al., 1999). All species, but CO and OCS, exhibit column density profiles within 3 AU from the Sun which are consistent with production from the nucleus.

Comet Hale-Bopp was one of the first opportunities to investigate the brightness distribution of rotational molecular lines with interferometers working at millimetre wavelengths. The interferometer configurations used for Hale-Bopp observations provided maps with angular resolutions from 2–4" (IRAM Plateau de Bure, OVRO) to 9" (BIMA array), corresponding to cometocentric distances of 2000 to 9000 km near perihelion. Interferometric maps of rotational lines of CO, HCN, H_2S, CS, SO, H_2CO, HNC, DCN, HDO, CH_3OH were obtained (Blake et al. 1999; de Pater et al., 1998; Veal et al., 2000; Wink et al., 1999; Wright et al., 1998; Wink et al., 1999; Woodney et al., 2002). Many of them have not been yet studied in details. Extended sources are clearly suggested for H_2CO and SO (Wink et al., 1999). Parent molecule distributions explain correctly HCN and H_2S maps (de Pater et al., 1998; Veal et al., 2000; Wink et al., 1999; Wright et al., 1998).

The steep heliocentric evolution observed in comet Hale-Bopp for H_2CO (Biver et al., 1999a) — a species for which the extended nature is well established — showed that clues on the production mechanisms of molecular species could be obtained from their gas production curves. An example of distributed production mechanism causing steep production curve is the chemistry involving HCN and H and leading to the creation of HNC (Section 5). One may also expect steep production curves if the molecules are released by grains from a decomposition process which is r_h dependent. Besides H_2CO, HNC, and OCS (see detailed discussion below), CS also showed a steep production curve (Biver et al., 1999a).

The evidence for extended sources in comet Hale-Bopp can be searched for in the radio line profiles which trace the velocity field of the molecules. At $r_h > 3.5$ AU, CH_3OH, H_2CO and OH exhibited line shapes quite different, in terms of Doppler shift and width, from those of CO. This was interpreted as reflecting the sublimation of these species from extended sources, likely icy grains, while CO was primarily released from the nucleus (Biver et al., 1997; Womack et al., 1997). Closer to the Sun, comet Hale-Bopp exhibited a large collisional region (a few 10^5 km at perihelion according to Combi et al., 1999), excluding any peculiar outflow velocity for molecules released in the collision zone, whatever their production mechanisms. There is no observational report in the literature of significant differences between H_2CO/CO and HCN/H_2S outflow velocities (Biver et al., 1999a).

Finally, the presence of extended grain sources of radicals in comet Hale-Bopp is proposed to explain the morphology of the CN, OH and C_2 jets (Lederer & Campins 2001, 2002), and the excitation state of C_2 into the jets (Laffont et al., 1999).

3.1. CO AND OCS

The $v = 1 - 0$ ro-vibrational lines of CO near 4.7 μm were observed by long-slit spectroscopy in the heliocentric range 0.93–4.1 AU (DiSanti et al., 1999, 2001). Their spatial profiles differ from those observed for H_2O and dust infrared emission (Fig. 1). They can be explained by the presence of a distributed CO source well developed at 6–7 $\times$ 10^3 km from the nucleus and contributing to half the total $Q_{\rm CO}/Q_{\rm H_2O}$ = 0.24 production ratio. The distributed source was present only within $r_h < 1.5$ AU and its turn-on on the brightness profiles coincided with a sharp increase of total CO production. We believe that this second line of evidence for distributed CO production is not very solid since many species, including OH, exhibited similar enhanced production at 1.5 AU inbound (Biver et al., 1999a). Additional constraints on CO origin are expected from the CO interferometric maps obtained at 115 and 230 GHz with IRAM Plateau de Bure (Henry et al., 2002). These spectral maps revealed the presence of a strong CO spiralling jet issued from the equatorial zones of comet Hale-Bopp's nucleus, and releasing 40% of the total number of CO molecules in the coma. Whether the interpretation of these maps requires extended CO production is in study (Henry, *personal communication*).

Production from an extended source is suggested for OCS on the basis of the spatial brightness profiles of its ν_3 ro-vibrational lines

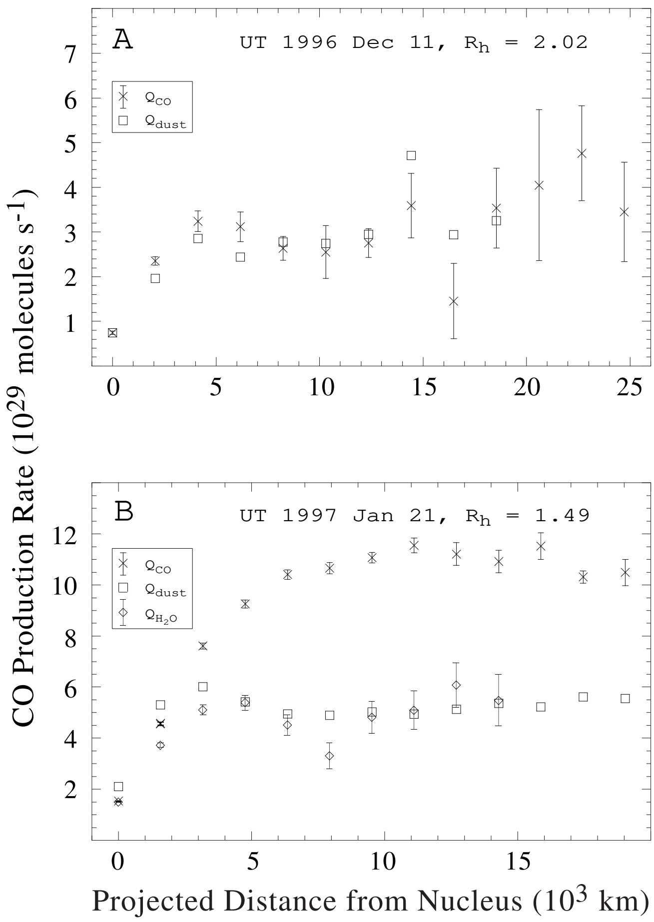

Figure 1. Production rates of CO, H_2O and dust as a function of line-of-sight distance from nucleus derived from infrared long-slit spectroscopy in comet Hale-Bopp (DiSanti et al. 2001). At $r_h = 2$ AU (top), the production rates of dust and CO do not increase with distance to nucleus, showing that these species are released from (or close to) the nucleus. At $r_h = 1.5$ AU (bottom), in contrast with H_2O and dust, the production of CO increases with nucleus distance up to about 10 000 km, indicating a distributed source of CO.

recorded in April 1997 (Dello Russo et al., 1998). The extended source would contribute to 70% of the total OCS production. Woodney (2000) inferred a much steeper production curve for OCS than for H_2S within $r_h = 2$ AU, which would also argue for an extended OCS production.

3.2. H_2CO

The interferometric observations of the 225 GHz line of formaldehyde at IRAM provide clear evidence for H_2CO being essentially released by an

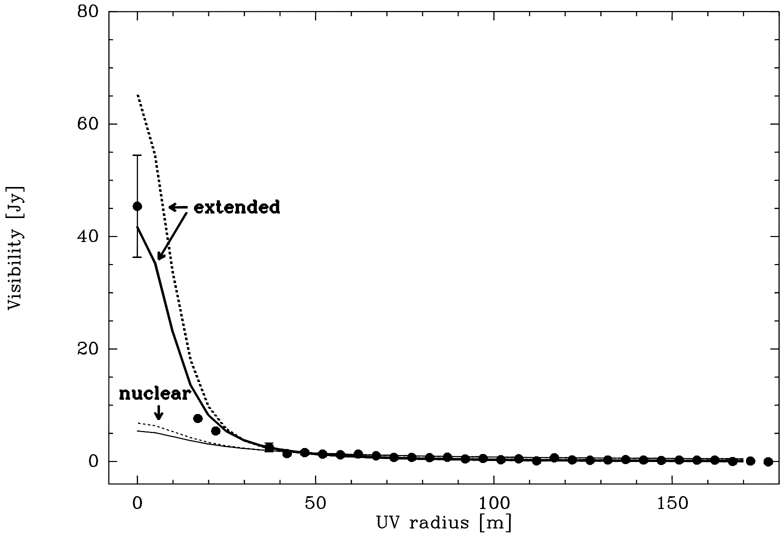

Figure 2. IRAM Plateau de Bure observations of the H_2CO 225 GHz line in comet Hale-Bopp on March 16, 1997. Visibility as a function of UV radius (i.e., projected baseline length). *Filled circles with error bars*: observations; *thin solid line*: Haser parent distribution and pure thermal excitation at $T = 110$ K; *thin dotted line*: Haser parent distribution with excitation model including collisions with electrons and radiative excitation; *thick solid line* and *thick dotted line*: the same for a Haser daughter distribution with $L_p = 7000$ km (Biver et al. 1999b).

extended source in comet Hale-Bopp (Wink et al., 1999). Figure 2 shows the cross-correlated signals of the antenna pairs (also called visibilities) as a function of baseline length. The data drop more rapidly to zero, when the baseline increases, than expected for a Haser parent distribution, which indicates a less peaked distribution. The observations can be well fitted by a daughter distribution with L_p similar to those determined in comets Halley and Hyakutake.

H_2CO exhibited a very steep ($\sim r_h^{-4.5}$) production curve all along the $r_h = 1$–4 AU range (Biver et al., 1997, 1999a). For comparison, most molecular species (e.g., H_2O, HCN, CO, H_2S, CH_3OH) displayed production curves with an average dependence between $r_h^{-2} - r_h^{-3}$ (Biver et al., 1999a; Dello Russo et al., 2000; DiSanti et al., 2001). Still more meaningful, the H_2CO/HCN production ratio varied in $r_h^{-2.1}$ in the 1.5–4 AU r_h range (Biver et al., 1999a).

3.3. HNC

Hydrogen isocyanide was first detected in comet C/1996 B2 (Hyakutake) with an HNC/HCN mixing ratio of 6% (Irvine et al., 1996). Observations in comet Hale-Bopp conducted at several radio telescopes revealed an HNC/HCN ratio increasing progressively from less than 3% up to ~20% when the comet approached the Sun (Biver et al., 1997, 1999a; Irvine et al. 1998a, 1999). The HNC/HCN ratio varied as r_h^{α} with α estimated to -2.5 by Biver et al. (1999a), and between -2.2 and -0.9 by Irvine et al. (1998b).

The HNC J(1–0) line was observed with the IRAM Plateau de Bure interferometer. A preliminary comparison with the brightness distribution of the HCN J(1–0) line would suggest production of HNC in the coma, in contrast to HCN (Wink et al., 1999).

3.4. SO

SO was detected in comet Hale-Bopp at several radio telescopes (Lis et al., 1999; Bockelée-Morvan et al. 2000; Woodney, 2000). Its 6_5–5_4 line at 219.949 GHz was imaged with the IRAM Plateau de Bure interferometer (Wink et al., 1999). The measured visibilities as a function of baseline length strongly deviate from the curve expected for a parent molecule distribution (see Despois, 1999), as observed for H_2CO (Fig. 2). There is clear indication for an extended source distribution for SO.

Photolysis of SO_2 is believed to be the main production mechanism of SO. The SO production rates determined in the assumption of production from SO_2 are in good agreement with contemporaneous SO_2 production rates (Bockelée-Morvan et al. 2000), taking into account model uncertainties. Improved excitation models are required to attribute the somewhat higher SO production rates to the presence of sources of SO other than SO_2 molecules (Bockelée-Morvan et al. 2000).

The photodissociation rate of SO_2 is somewhat uncertain. Values differing by a factor of 2 can be found in the literature (see references in Bockelée-Morvan et al. 2000). The parent scale length required to fit the SO interferometric data is consistent with the range of estimated SO_2 scale lengths (in Fig. 7 of Despois, 1999, the dotted dashed line fitting the data corresponds to $L_p = 14\,000$ km, in agreement with the SO_2 photorate of 1.4×10^{-4} s^{-1} of Kim & A'Hearn, 1991).

4. Models

4.1. Chemistry in the coma

Chemical models of chemistry in cometary comae will not be reviewed here (see Rodgers & Charnley 2002a, 2002b for a recent review). Such models are crucial for evaluating the density distribution of molecules and to relate the observed column densities to molecular production rates. There is still a need for photolytic and reaction rates.

Given the small abundances of minor species (such as some CHO species or nitriles) observed in comet Hale-Bopp, it is legitimate to wonder whether such species could be synthesized through chemical reactions in the coma, rather than sublimated from nucleus ices. Such processes could be much more efficient in a "big" comet like Hale-Bopp, which has a large collisional coma.

Recently, Rodgers & Charnley (2001a) evaluated the importance of such a process and showed that it is not significant. Following their chemical model, species such as HCOOH, CH_3CN or $HCOOCH_3$ could only be produced with abundances $\approx 10^{-6}$ relative to water in comet Hale-Bopp close to perihelion, more than two orders of magnitudes less than what is observed. Similarly, Canaves et al. (2002) showed that NS could not be formed either from known gas-phase cometary molecules.

4.2. Molecules from grains

Some molecules such as carbon monoxide and formaldehyde are produced in huge amounts from distributed sources (Section 3). They obviously cannot come from the degradation of known volatile species. There is a consensus that such species would be released from organic grains, such as those which were observed *in situ* in comet Halley. However, we have to admit that there is still no satisfactory quantitative explanation for the desorption mechanisms.

1. Sublimation of icy grains

   Such a process certainly occurs to some extent. However, the predicted lifetimes of icy grains at $r_h \approx 1$ AU are so small that the resulting distributed source would be very difficult to distinguish from a nuclear source by remote sensing. On the other hand, it would be surprising that cometary icy grains were producing extended sources of CO and H_2CO with the observed scale length, without producing also an extended source of water (cf. Fig. 1).

2. Thermal desorption or sublimation of (semi) volatiles; pyrolysis of large molecules

   Lamy & Perrin (1988) proposed that superheated tholin grains could be a source of organic molecules within the coma. Polyoxymethylene (POM) was first invoked to explain the production of formaldehyde and other species within the coma of 1P/Halley (Huebner et al. 1987). The thermo-degradation of POM mainly produces H_2CO. The photo-degradation of POM produces in addition CO, CO_2, and small quantities of various CHO species (Cottin et al. 2001). However, the photo-degradation of POM is much less efficient than its thermo-degradation, so that POM could explain (at least qualitatively) the distributed source of H_2CO, but not that of CO. In order to explain the latter, POM would have to release H_2CO in a much higher quantity than what is observed. On the other hand, the thermo-degradation of POM critically depends upon the temperature. A quantitative modelling of this process as a function of heliocentric distance has not been done yet, but it is unlikely that this process could explain the production of H_2CO observed at large r_h (Biver et al. 1999a).

3. Photolysis by UV photons or sputtering by energetic particles

   These processes are very inefficient, because the cross section per molecule in grains is much smaller than in the gas phase.

Obviously, there is a need for a close collaboration between laboratory physicists and cometary observers and modellers to understand these processes.

5. Specific issues

5.1. The HNC/HCN ratio

First observed in comets Hyakutake and Hale-Bopp (see Section 3), HNC was subsequently detected in several weaker comets (C/1999 H1 (Lee), C/1999 S4 (LINEAR), C/2001 A2 (LINEAR); Biver et al. 2002). In the case of comet Hale-Bopp, the increase of the HNC/HCN ratio with the increase of activity of the comet as it approached the Sun, together with the extension of the HNC source suggested by mapping observations, were used as an argument in favour of chemical synthesis of HNC (Irvine et al. 1998a; Rodgers & Charnley 1998). Models including reactions with fast hydrogen and the intermediate ion $HCNH^+$

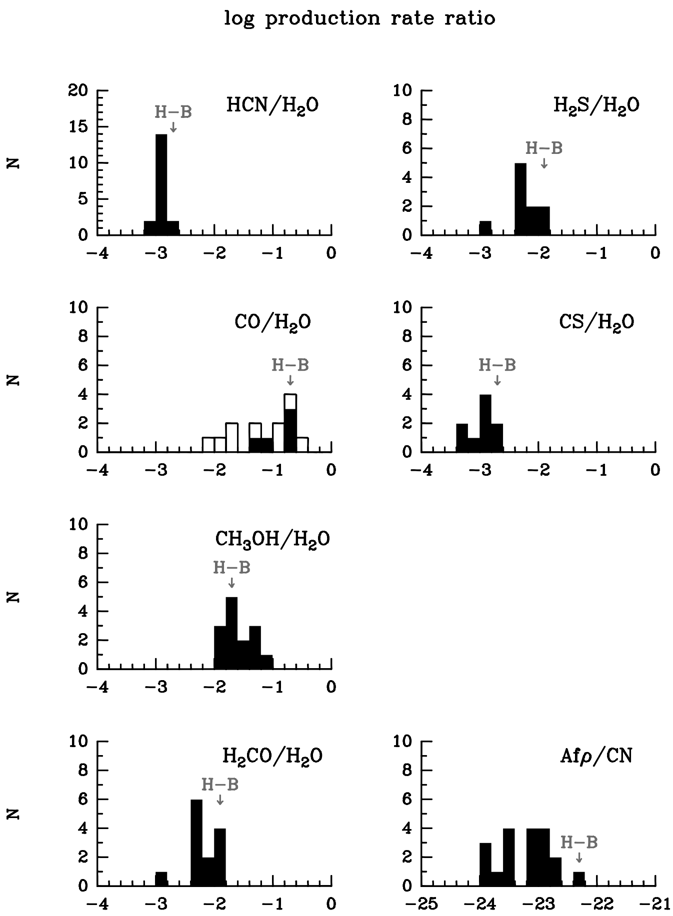

Figure 3. Histograms of relative production rates for a sample of 24 comets observed at radio wavelengths (from Biver et al. 2002). For CO, the radio data have been completed by UV and infrared data (white histogram). The $Af\rho$/CN histogram is from observations in the visible. The place of comet Hale-Bopp in each histogram is indicated.

could then reproduce the HNC/HCN ratio. But they could not explain the presence of HNC in comet Hyakutake and other *weak* comets (Rodgers & Charnley 1998, 2001b).

Methanimine (CH_2NH) could be a plausible parent for HNC. However, this seems to be ruled out by the upper limit derived for this molecule (Table II). Rodgers & Charnley (2001b) argued that HCN polymers could be a source for HNC. Laboratory experiments should assess whether or not such polymers could produce HNC when they degrade in cometary conditions. If they do, they would likely contribute also to an extended source of HCN, which does not seem to be observed.

5.2. The ortho-to-para ratio

The *ortho* and *para* (or A and E) states of molecular species with identical H-atoms may be considered as chemically different. The ortho-to-para ratio (OPR) is thus a testimony of the chemical history of the species (Crovisier 1984; Mumma et al. 1993). For cometary water, the OPR was found to be significantly different from the statistical weight (high temperature approximation) limit in comets 1P/Halley (Mumma et al. 1993), Hale-Bopp, and 103P/Hartley 2 (Crovisier et al. 1997, 1999).

But the actual meaning of this ratio and of the corresponding spin temperature ($\approx$ 30 K) is still an open question. Is it the formation temperature of water, or the re-equilibration temperature within the nucleus, or the result of fractionation during condensation or sublimation of water? In any case, a change of the water OPR following collisions or chemical reactions within the coma seems to be excluded.

The study of the OPR of other cometary species (CH_4, H_2CO, CH_3OH, NH_3) is still preliminary. The prospect to deduce the OPR of a parent molecule from that of its dissociation products was recently brought up. Kawakita et al. (2001, 2002) inferred the OPR of NH_3 from their measurement of the OPR of the NH_2 radical. It corresponds to a spin temperature of 28 K for comet C/1999 S4 (LINEAR).

5.3. The D/H ratio

The D/H ratio was measured spectroscopically in the H_2O and HCN molecules in comets Hyakutake and Hale-Bopp (Bockelée-Morvan et al. 1998; Meier et al. 1998a, 1998b). Rodgers & Charnley (2002a) have shown that the D/H ratio cannot be affected by chemical reactions within the coma. The D/H ratio is thus of pristine nature and can be used as a touchstone for physico-chemical models of the formation of cometary material (Bockelée-Morvan et al. 1998; Drouart et al. 1999; Mousis et al. 2000; Hersant et al. 2001).

5.4. Was comet Hale-Bopp “typical”?

According to the taxonomy of A’Hearn et al. (1995), comet Hale-Bopp was *typical* rather than *C-depleted.* How does this taxonomy, based upon an investigation of radicals from broad-band photometry , translates into genuine chemical diversity of cometary ices, is yet unclear. From their investigation of relative abundances of cometary parent molecules, Biver et al. (2002) found a large chemical diversity, but they could not identify different classes of comets, or any correlation with their dynamical origin.

Figure 3 shows the place of comet Hale-Bopp in the distributions of relative molecular abundances from the sample of Biver et al. (2002). Although the comet fits into the histograms of all comets, it shows strong departures from the mean abundances: it is enriched in CO, H_2CO, H_2S and CS, but it is rather depleted in CH_3OH.

The same figure shows $Af\rho/Q_{\rm CN}$, which traces the dust/gas ratio. It shows how exceptional was the dust production of this comet. Also exceptional was the superheating of its dust grains and the intensity of its silicate feature. This can be attributed to the dust population being dominated by small-size particles (Williams et al. 1997; Mason et al. 2001).

6. Pending questions

The observations of comet Hale-Bopp have considerably enriched cometary science. But several old questions are still unanswered and new ones have emerged. Some of them, related to cometary chemistry, are listed below.

1. Which species are still to be discovered?

   About 25 cometary parent molecules are now known. There are certainly many more molecules to be detected at the 10^{-4}–10^{-5} abundance level, but we may wonder if we are missing important molecules at the 10^{-3} or more level.

   Figure 4 shows the cumulative histogram of detected species with relative abundances larger than a given value. According to the extrapolated power law drawn in this figure, one would expect 100 to 200 species to exist with abundances $> 10^{-5}$ relative to water, but such an extrapolation is admittedly highly hazardous.

2. Origin of distributed CO, distributed H_2CO?

   Given the importance of carbon monoxide in comets (both in the coma and in nucleus ices), the still unknown nature of the distributed source of CO is an irritating problem and perhaps one of the most challenging issues of cometary science.

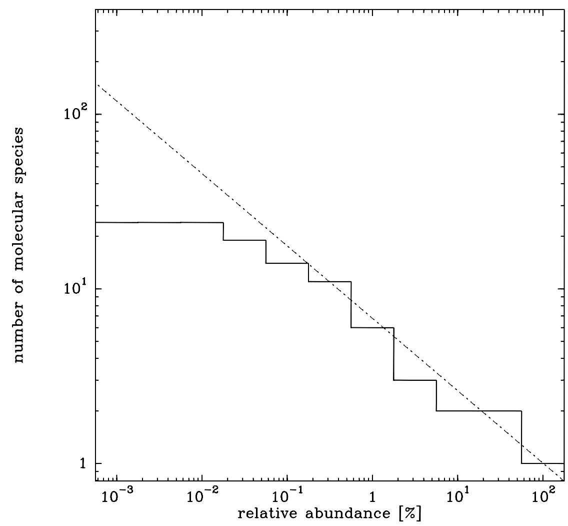

Figure 4. The number of detected molecular parent species with production rates, in percent relative to water, larger than a given abundance value (histogram). The dashed line is a guess of the true distribution. (From the data listed in Table I, deuterated species excluded.)

3. Nuclear versus distributed source of HNC?

   HNC is admittedly a minor species in comets. But the possibility to measure the HNC/HCN fairly reliably in several comets makes it a touchstone for our knowledge of cometary molecular processes.

4. Parent for the NS radical?

   The presence of the NS radical with significant abundance in the coma was *a priori* unlikely, given the elemental abundances of N and S. Only *exotic* parents can be invoked for this radical.

5. Origin of Na and Na tail?

   Not discussed above is the origin of cometary sodium, which showed such an obvious *third type* tail in comet Hale-Bopp (Cremonese et al. 1997; Wilson et al. 1998). The evidence for a distributed source of Na was presented (see also discussion by Combi et al 1997 and observations by Arpigny et al. 1998). However, no sodium-bearing parent molecule, or no efficient desorption mechanism from refractories could be found.

These questions could be answered by space exploration by a probe dedicated to the study of molecules in the coma, such as *Rosetta*, or by the remote study of another very bright comet, if one shows up in the meantime.

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