Physics and chemistry of comets: recent results from comets Hyakutake and Hale–Bopp

Answers to old questions and new enigmas

J. Crovisier[†]

Observatoire de Paris-Meudon, F-92195 Meudon, France

1996 and 1997 years were very prolific years for cometary studies. In March 1996, C/1996 B2 (Hyakutake), a medium-bright comet, passed at only 0.10 astronomical units (AU) from the Earth. On 1st April, 1997, C/1995 O1 (Hale-Bopp) passed at perihelion. This comet was 10 to 100 times brighter than comet Halley when compared at the same distance. It could be studied and monitored from its discovery in July 1995 as far as 7 AU from the Sun until its perihelion at 0.9 AU, where it was the object of extensive observations. It was thus possible to study these two exceptional comets with modern instrumentation covering the electromagnetic spectrum from radio to X-ray domains. Our knowledge of the composition and nature of comets has been transformed. New cometary molecules were observed, as well as isotopic species. New physical processes could be studied, owing to the large amounts of matter escaping from these objects, to the proximity of Earth allowing a detailed investigation of the region close to the nucleus (comet Hyakutake), or to the unusual physical conditions far from the Sun (comet Hale-Bopp).

Selected results of these observations, relevant to the chemistry and physics of molecules and grains, are discussed. It is shown that whereas some old problems are now solved, new ones have emerged. The needs for laboratory data and theoretical work are pointed out.

1 Introduction

We were recently presented with two exceptional comets. In March 1996, comet C/1996 B2 (Hyakutake) passed at only 0.1 astronomical units (AU) from the Earth. In spring 1997, comet C/1995 O1 (Hale–Bopp) made its closest approach to the Sun (0.9 AU). This comet was releasing 10 to 100 times more gas and dust than comet Halley and is thus among the brightest comets ever recorded. The early discovery of comet Hale–Bopp in July 1995, its long period of visibility, the availability of new telescopes equipped with state-of-the-art instrumentation, made possible the organization of very productive observations which revolutionised our knowledge of comets. For an assessment of cometary science before these two events, the reader is referred to the reviews of Festou *et al.*¹ and Mumma *et al.*²

The aim here is not to review all the results obtained on these comets, but to highlight and discuss some of those relevant to molecular processes. We will try to show that whereas some old problems are solved, new questions are now raised. It is remarkable that more than one century after their discovery in the visible spectrum of comets, the origins of the CN and C_2 cometary radicals are still subjects of debate.

† E-mail: crovisie@obspm.fr

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2 New molecules

2.1 New cometary molecules

New molecules have been detected from radio observations in the millimetre and submillimetre ranges.^{3,4} Besides single-dishes such as the Institut de Radio Astronomie Millimétrique (IRAM) 30 m, the Effelsberg 100 m, the James Clerk Maxwell Telescope (JCMT) 15 m, the National Radio Astronomy Observatory (NRAO) 12 m and 42 m, and the Caltech Submillimeter Observatory (CSO) 10 m telescopes, radio interferometers [the IRAM and Berkeley-Illinois Millimeter Array (BIMA)] used in the single-dish mode, where all antenna are used in parallel, proved to be efficient in this search.⁵⁻¹² The radio studies were complemented by high-resolution ground-based IR spectroscopy (especially with IRTF/CSHELL).¹³⁻¹⁶ The infrared space observatory (ISO), which unfortunately could not observe the comet close to the Sun, did not detect any new gas-phase molecules, but was able to trace H₂O, CO₂ and CO and to analyse the composition of cometary dust.¹⁷ No new species have yet been reported in the UV or in the visible, but many unidentified lines have now been spotted in the visible.¹⁸ The total number of molecules, radicals and molecular ions observed in comets is now one third of those observed in the interstellar medium.

For a review on cometary volatiles prior to the observations of Hyakutake and Hale–Bopp, see ref. 19. Table 1 gives a list (adapted from ref. 4; see also ref. 3) of the molecules observed in comets Hyakutake and Hale–Bopp, with the state-of-the-art evaluations of their abundances. Most of these values must be considered as preliminary and will be refined in the future as the observational data is further processed and analysed. Not listed are molecules searched for, but undetected. Stringent upper limits could be put on the abundances of many of them such as methanimine (CH₂NH), ketene (H₂CCO), ethanol (C₂H₅OH)...

Are there still missing molecules? With the definite detection of ammonia^{5,12} and of methane and hydrocarbons,^{13,14} one might think that all abundant volatiles (*e.g.* with abundances larger than *ca.* 1%) have now been identified. Water still appears to be the dominant volatile, representing *ca.* 75% by number (or 64% by mass) of the molecules sublimed from nuclear ices. O_2 , N_2 and H_2 are still elusive species; no significant upper limit could be obtained because of the lack of strong lines or bands of these non-polar, symmetric molecules that could be searched for. Therefore, we do not know to what extent these very volatile molecules could be trapped in cometary ices.

Table 1 suggests that there is no limit to the complexity of cometary molecules, but that their abundances decrease with increasing complexity. In parallel, complex species are heavy molecules with their population distributed over many rotational levels, even at the low temperatures of cometary gases; their emission spectra are thus spread over a large number of lines. Hence, really complex molecules, such as glycine, might exist in comets, but the prospects for their detection by remote sensing are grim.

Isotopic ratios, for which accurate determinations are now available from radio observations, will not be discussed here. Let us just mention that the [D]/[H] ratio is highly enriched in the water of comets Hyakutake and Hale-Bopp $(3 \times 10^{-4}, cf.$ the 'cosmic' value of 1.5×10^{-5}),^{20,21} confirming the high value previously observed in comet 1P/Halley by *in situ* mass spectroscopy. The [D]/[H] ratio is still higher (2×10^{-3}) in the HCN molecule observed in comet Hale-Bopp.²² However, other isotopic abundances for carbon, nitrogen and sulfur are 'normal'.²³

2.2 Unidentified lines

Unidentified lines have been noted in the visible, IR and even radio spectral ranges. Some in the visible domain, were listed and discussed by Arpigny,^{24,25} Brown et al.²⁶

Table 1	Cometary	parent	molecules	observed	in	comet	Hale-
Bopp with their abundances							

molecule	relative abundance	observational technique
H ₂ O	100	IR
CŌ	20	radio, IR, UV
CO ₂	6	IR^a
CH_{4}^{2}	<i>ca.</i> 1	IR
C,H,	<i>ca.</i> 0.5	IR
$\tilde{C_2H_6}$	ca. 0.5	IR
ĊĤ₃ŎH	2	radio, IR
H ₂ ČO	<i>ca.</i> 1	radio
НČООН	0.05	radio
HCOOCH ₃	0.05	radio
NH ₃	0.6	radio
HCŇ	0.2	radio, IR
HNC	0.03	radio
CH ₃ CN	0.02	radio
HC ₃ N	0.02	radio
HNCO	0.1	radio
NH ₂ CHO	0.01	radio
H ₂ S	1.6	radio
SŐ	0.6	radio
SO_2	0.15	radio
OCS	0.5	radio, IR
CS_2	0.2	UV, radio ^{b}
H ₂ CS	0.02	radio
$\tilde{S_2}$	0.005	UV ^c

Abundances are given by number, relative to water. Table adapted from ref. 4. ^{*a*} Observed by ISO at 4.6 and 3 AU. The CO_2/CO ratio was assumed to be the same at 1 AU. ^{*b*} Assuming that CS is coming from CS_2 . ^{*c*} Not observed in comet Hale–Bopp. The listed abundance pertains to comet Hyakutake.

[559 lines from comets 109P/Swift–Tuttle and C/1990 K1 (Levy)], and Morrison *et al.*¹⁸ (18 lines from comet Hyakutake). Others, coming from high-resolution spectral surveys of comets Hyakutake and Hale–Bopp, will need some time before they are analysed and published. It is likely that many may be attributed to radicals and ions, for which spectral data are still poor. For instance, a better knowledge of the spectrum of NH₂ led to the assignation of a large number of previously unidentified lines.²⁵ Could some of these unidentified lines have the same origin as the diffuse interstellar bands (DIBs)? No systematic investigation of this idea has, to our knowledge, been undertaken. A cursory inspection of available catalogues of unidentified cometary lines^{18,26} with comparison with DIB data bases (*e.g.* ref. 27) does not reveal any obvious correspondences other than what could be expected by chance. Note, however, that the formation mechanisms of DIB and cometary lines are probably quite different: absorption for the former, fluorescence emission for the latter. Thus, the same molecules from different sources could show signals at different wavelengths.

2.3 SO, SO₂ and S₂

The detection of several radio lines of SO and SO_2^{6} came as a surprise, because very stringent upper limits were obtained from the analysis of UV spectra of preceding

comets (ca. 4×10^{-4} and 10^{-5} relative to water for SO and SO₂, respectively²⁸). The abundances of these two molecules are now found to be of the order of 0.6 and 0.15%, respectively (Table 1), which makes them a significant depository of cometary sulfur. Interferometric observations of Hale–Bopp showed that SO is a secondary species, presumably coming from the photodissociation of SO₂.⁶ The preliminary estimates, however, lead to Q[SO] larger than $Q[SO_2]$. The lifetimes of SO and SO₂ are poorly known (published values differ by large factors). The excitation of these molecules is also not well known: UV excitation may be an important factor (but the previous work of Kim and A'Hearn²⁸ may have to be reconsidered, since it led to production rate upper limits in strong conflict with those observed in comet Hale–Bopp). There is, thus, an obvious need for SO and SO₂ UV molecular data and improved modelling of the fluorescence of their electronic bands in the UV.

The S₂ molecule was first detected from its near-UV bands in comet C/1983 H1 (IRAS–Araki–Alcock) when it passed at only 0.031 AU from the Earth. It could not be observed in subsequent comets, except recently in comet Hyakutake.²⁹ This confirms that this molecule can only be observed in comets passing very close to the Earth, owing to the very short life time of S₂ (*ca.* 500 s). What is the origin of cometary S₂? It was argued³⁰ that it could be formed following photoprocessing of H₂S in interstellar ices. However, this process also creates SO and SO₂ and was discarded at that time because of the very low upper limits put on the abundances of these species from UV observations. In view of the detection of SO and SO₂ in comet Hale–Bopp, this hypothesis has now to be reconsidered.

2.4 Molecular ions

Molecular ions have been observed for the first time at radio wavelengths in comet Hale–Bopp: $\rm CO^+$, already well known in cometary ionic tails from visible spectroscopy, and the new ions $\rm HCO^+$ and $\rm H_3O^{+,9-10}$ The observations of the radio line shapes will be very useful for the study of the kinematics of the ions and of the formation of ionic coma from neutral coma. Another important cometary ion, $\rm H_2O^+$, also well studied from its visible spectrum in the ionic tails, has not yet been observed in the radio. Its radio rotational lines have not yet been observed in the laboratory and their frequencies are not known precisely. Its lower energy lines (expected to be the strongest in comets) are not within the frequency range accessible from the ground: they could be a goal for future space submillimetre radio telescopes such as FIRST.

2.5 Need for molecular data

Photodissociation rates. Retrieving molecular production rates and abundances from observed signals requires knowledge of the photodissociation rates which govern the molecular space densities and their scale lengths. Several of them are poorly known (see above for SO and SO₂) or even unknown: among recently identified parent molecules, this is the case for H_2CS and NH_2CHO . (For reviews see ref. 32 and 33.)

Water production rates. Water appears to be the dominant species among cometary ices. It is thus usual to report abundances of other species relative to water (Table 1). Ironically, the determination of water production rates is still a problem and one of the main sources of error in the determination of relative abundances. Water is very difficult to observe from the ground: rotational lines and fundamental vibrational bands are blocked by telluric absorption. Available high-altitude or space observations of water in comets are rare [IR spectrometer (IKS) on the Vega probes;^{34,35} Kuiper Airborne Observatory (KAO);^{36,37} IR space observatory (ISO)^{17,38}] and cannot provide a detailed monitoring of the water production rates in comets. Mainly, one has to rely on secondary indicators such as the radio or UV lines of OH or the forbidden lines of OI.

Quite recently, the possibility of observing the $v_1 + v_2 + v_3 - v_1$ hot band of water, at 1.94 µm from the ground arose,³⁹ (see also ref. 14). This band is emitted as one step in the complex fluorescence cascade which follows vibrational excitation of water by the solar radiation field. However, the emission rate of this band is not precisely known, because there is no laboratory measurement of its band strength. Present models rely on the assumption that this band strength is the same at that of the corresponding 'cold' band $v_2 + v_3$.¹⁴ Hence, imprecise determinations of water production rates from this band, which is otherwise relatively easy to observe.

3 C₂ and C₃ are no longer 'orphan molecules'

For several decades, cometary specialists tried to guess the identity of the parent molecules, directly sublimed from the nucleus, responsible for the daughter molecules observed in the visible spectra of comets. Having no access to cometary spectra outside the visible window, parent molecules could not be observed directly. The C_2 and C_3 radicals remained, for a long time, orphan molecules for which no parent could be found.

This is no longer the case. There are now several two-carbon atom molecules identified from radio and IR spectroscopy: C_2H_2 , C_2H_6 (both with an abundance of *ca*. 0.5%), CH₃CN, HCOOCH₃ (with much smaller abundances). One three-carbon atom molecule has even been found: HCCCN.

The C₂ abundance in comets is of the order of 0.004 (as estimated for 'typical comets'⁴⁰). Thus, the photodissociation of C₂H₂ or C₂H₆ could provide the observed C₂ in sufficient amount. The details of the photodissociation processes are not well known. The production of C₂ from C₂H₂ is presumably a two-step process, the intermediate product being C₂H. The production of C₂ from C₂H₆ might involve more steps, an intermediate product being C₂H₂.³³ In order to evaluate C₂ production quantitatively from these molecules and to compare this value with the observed C₂, one would need to know the precise yields of C₂, as well as the excess energies at each step of the photodissociation process, because these excess energies are converted to the ejection velocities of the photo-fragments and affect the C₂ spatial distribution.

Combi and Fink⁴¹ have examined in detail the spatial distribution of C_2 in comets. It is well known that the density profiles of C_2 are flatter than expected from simple photodissociation from a parent molecule. This has been invoked as a clue to the production of C_2 directly from dust grains with organic mantles. They found, however, that the spatial distribution of C_2 can be consistent with two- or three-step photodissociation, provided that proper ejection velocities of the photo-fragments have been taken into account. They remark that the dependence of this distribution on heliocentric distance r, is not consistent with such a process and would be better explained by a dust source. However, they have not investigated the case for multiple parent molecules: if various parent molecules of different scale lengths are sublimed from the nucleus with different sublimation laws, the r-dependence of the C_2 molecule space distribution may be tricky.

Sorkhabi *et al.*⁴² have obtained high-resolution spectra of the $D^{1}\Sigma_{u}^{+}-X^{1}\Pi_{g}^{+}$ Mulliken system of C₂ (around 2413 Å) in comet Hyakutake, using the space telescope to probe the near-nucleus region. They attributed the spectrum to that of C₂ in nascent conditions and found that it has a hot vibrational and rotational excitation, remarkably similar to that observed in the laboratory from the photodissociation of C₂H₂. In our view, this is not proof that C₂ is coming from acetylene alone: photodissociation of C₂H₆ and C₂H₄ (another molecule which, although not identified, is likely to be present in comets) proceeds in several steps, one of them being *via* C₂H₂.³³ In conclusion, we think that we now have convincing evidence that cometary C_2 is coming mainly from hydrocarbons. Whether or not all the observed C_2 can be explained by the presently identified hydrocarbons would need detailed knowledge of the photolysis of hydrocarbons, with the yields of the various photolytic channels and the ejection velocities given to the photo-fragments, for a quantitative evaluation of the C_2 production and spatial distribution. The existence of a dust source for C_2 is questionable. The problem of the dust source for radicals will be further discussed in Section 6.

4 The 3.2–3.6 μm band

An important discovery of the observing campaign of comet P/Halley was that of a strong emission band around 3.2–3.6 μ m in its IR spectrum.^{34,35} There is little doubt that this band, characteristic of the C—H-stretching mode, corresponds to carbonaceous molecules. But which ones? Such an emission could arise from the fluorescence of gas-phase molecules, as well as from thermal emission of organics in the mantle of small cometary grains.

The problem was solved, in part, by the unambiguous identification of methanol through its radio lines in comets C/1989 X1 (Austin) and C/1990 K1 (Levy), with an abundance of a few per cent. Methanol has a vibrational band (v_3) at 3.52 µm which is identified as a discrete band in the IR cometary spectra of several comets, and two bands $(v_2 \text{ and } v_9)$ around 3.3–3.4 µm. Using fluorescence models and the production rates retrieved from radio observations, the v_3 band fits well with the 3.52 µm emission; the v_2 and v_9 bands, however, only partly account for the 3.2–3.4 µm emission (see the review by Bockelée-Morvan *et al.*)⁴³ They estimate that, to account for the full 3.2–3.6 µm emission, additional gas-phase molecules are necessary, with a production rate comparable to that of methanol, if their fluorescence rates are similar to that of methanol.

A reassessment of the nature of this band has to be made in view of the recent detection of several new molecules which have strong bands in this domain. Table 2 lists the contribution of vibrational bands of identified cometary molecules (Table 1) to the $3.2-3.6 \mu m$ emission. Table 2 shows that methanol is still the major identified contributor to the emission. Hydrocarbons are also important. Formaldehyde would come second to methanol. It is not, however, definitely identified in cometary IR spectra (see discussion in ref. 44). Cometary formaldehyde is believed to be a secondary species coming from a distributed source: the IR spectra which are taken with a small aperture are just not sensitive to this secondary species.

Unidentified lines have been reported in this spectral domain from the IRTF/ CSHELL high-resolution observations. With the discovery of three hydrocarbons showing a large two-carbon to one-carbon ratio, much larger than expected from thermal equilibrium chemical reactions, one can expect that a large number of other hydrocarbons will also be present. A sharp feature has also been observed at $3.425 \,\mu\text{m}$ in the spectrum of 109P/Swift–Tuttle.⁴⁵ No clear identification has been found for this feature (to our knowledge, this feature has not been reported in comets Hyakutake or Hale–Bopp).

It is clear that there are still molecules to be identified in this spectral domain. The high-resolution spectra have to be compared with synthetic molecular spectra. For such a modelling, band strengths and band structures are needed; they are only available for the fundamental bands of the simplest molecules. Although Table 2 (with the proviso that other putative molecules are to be added) suggests that gas-phase molecules alone could account for all the observed emission, a contribution from thermal emission of the organic mantle of cometary dust grains cannot be excluded.

A controversial result from the P/Halley observations was the identifications of two polycyclic aromatic hydrocarbons (PAHs) (naphthalene and phenanthrene) in its near-UV spectrum observed by Vega-TKS.^{46,47} These identifications were based on

			$\sigma/$	g/	$\Sigma g X /$
molecule	X	band	cm^{-1}	10^{-4} s^{-1}	10^{-6} s^{-1}
main contributors					
CH_4	0.01	V ₃	3019	4.0	4.0
C,H,	0.002	V3	3295ª	1.7	(0.85)
C_2H_6	0.006	v_7	2969	7.2	3.6
H_2CO	0.01	v ₁	2782	3.9	8.5
-		v_5	2843	4.6	
CH3OH	0.02	<i>v</i> ₂	2999	1.9	13.8
		v_3	2844	1.5	
		<i>v</i> ₉	2970	3.5	
total					29.9
secondary cont	ributors				
NH ₃	0.006	v_1	3337 ^a	0.34	(0.32)
-		v ₃	3444 ^a	0.20	
HCN	0.002	v ₃	3311 ^a	3.5	(0.7)
HNC	0.0003	v_1	3653 ^a	22.	(0.7)
HC ₃ N	0.0002	v_1	3327 ^a	8.6	(0.17)
CH ₃ CN	0.0002	v_1	2954	0.15	0.005
		<i>v</i> ₅	3009	0.10	
HCOOH	0.0005	<i>v</i> ₂	2942	1.9	0.1
HCOOCH ₃	0.0005	v_1	3045	?	
		<i>v</i> ₂	2969	?	
		<i>v</i> ₃	2943	?	
		v ₁₆	3012	?	
NH ₂ CHO	0.0001	?	?	?	
H_2CS	0.0002	v_1	2971	?	
		v ₅	3025	?	

Table 2 Contribution of molecular fluorescence bands to the 3.2–3.6 μm spectral range

X: molecular abundance relative to water. σ : wavenumber. g: fluorescence rate at 1 AU from the Sun (only resonant fluorescence of fundamental vibrational bands is considered here). ^a Below the 3.2–3.6 µm spectral range.

low-resolution spectra, which were observed quite near the nucleus. The presence of PAHs in comets is, indeed, suggested by the presence of a discrete band at $3.28 \ \mu m$ in the IR spectra of some comets. However, as discussed in ref. 43, the high abundances of naphtalene and phenanthrene retrieved from the TKS data do not match the more modest abundances for all PAHs that can be constrained from the IR spectra. The close approach to Earth of Hyakutake and the high matter-production rates of Hale–Bopp gave potentially a unique opportunity to solve this problem. To our knowledge, no report on the presence of PAHs in these comets, either from the near-UV or the IR, has yet been provided.

5 Comparison with interstellar ices

Cometary ices and interstellar ices are two models of cosmic material worthy of a detailed comparison. Following a now popular theory proposed by Greenberg,⁴⁸ comets may have formed from unaltered interstellar grains. Such a comparison would thus provide a critical test for this theory.

Table 1 shows our knowledge of the composition of cometary volatiles. The composition of ISM ices can be investigated by IR spectroscopy and has just been reassessed by ISO observations.^{49,50} It must be noted that two kinds of material are investigated in quite different ways which introduce their own bias:

Cometary ices were studied indirectly from their sublimation products. Highresolution spectroscopy of gas-phase molecules provides unambiguous identifications. Radio spectroscopy is very sensitive to some products and was able to sample very minor constituents. However, cometary ices may not have retained the most volatile species such as H_2 , N_2 or O_2 . Others, such as CO or CH_4 , may have been depleted, or are at least subject to sublimation fractionation, so that the abundances of volatiles observed in the coma (Table 1) are not directly representative of the initial cometary ice composition, but depend on the thermal history of comet nuclei and on the heliocentric distance at which the observation is made.

Interstellar ices are probed by observing the absorption spectra of strong IR sources deeply embedded in cold molecular clouds (protostars such as RAFGL 7009S or NGC 7538 IRS9). The spectroscopic features of ices are not so narrow as those of rotationally resolved spectra of gas-phase molecules and, in several instances, do not provide unambiguous identification. Moreover, the wavelengths of the features of ice mixtures usually vary with the composition, so that detailed comparison with laboratory measurements is needed. As a result, the proposed compositions of ISM ices vary from one author to another, not only in abundance values, but even in the proposed identifications. Only the major constituents are known: those with relative abundances of 1% or less appear to be difficult to observe.

Table 3 lists the composition of ISM ices, from several sources. The comparison with the cometary ices (from Table 1) is amazing. The major constituents, H_2O , CO, CO_2 , CH_3OH , H_2CO , CH_4 , which are relatively well known in both kinds of objects, are observed to have the same relative abundances within factors of two to four (which is no more than the relative dispersion from object to object). A much closer match is obtained if we admit that water is depleted in ISM ices compared to cometary ices.

A strong unidentified band at $6.85 \,\mu\text{m}$ is observed in interstellar ices.^{49,77} Hydrocarbons, methanol and HCO₂H may contribute, but the bulk of the band is still unidentified.⁴⁹ Carbonates and NH₄⁺ have also been proposed. Is there a corresponding species

species	interstellar ices	с	ometary ices
H ₂ O	=100	=100	
CŌ	10-40	20	
CO ₂	10	6	
CH ₃ OH	5	2	
H ₂ ČO	2–6 tent.	<i>ca</i> . 1	
HCOOH	3 tent.	0.05	
CH ₄	1–2	ca. 1	
other hydrocarbons	?	<i>ca</i> . 1	$C_{2}H_{2} + C_{2}H_{6}$
NH ₃	<10	0.6	
O ₃	<2	?	
XCN	< 0.5-10	0.37	nitriles + HNCO
OCS, XCS	0.2	0.7	$OCS + CS + H_2CS$
SO ₂	?	0.15	-
H ₂	<i>ca.</i> 1	?	
N ₂	?	?	
O ₂	?	?	

Table 3 Comparison of the compositions of interstellar and cometary ices

All abundances are given by number, relative to water. The abundances in interstellar ices are compiled from ref. 49–51. The abundances in cometary ices are from Table 1.

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in cometary ices? A band at 6.8 μ m was observed in P/Halley,⁵² but was not present in the spectra of comet Hale–Bopp observed at 4.6 and 3 AU.^{17,38}

Another puzzle is the identification of the so-called 'X–CN' band in the ISM ices at 4.62 μ m, close to the CO band at 4.67 μ m. This band corresponds to the stretching mode of many nitriles (hence the X–CN denomination), as well as to the Si–H-stretching mode. A more specific identification to the OCN⁻ ion has been proposed.⁵³ It is interesting to note that the HNCO molecule identified in comets Hyakutake and Hale–Bopp^{8,9} could indeed be produced by the release of OCN⁻ from cometary ices. However, the abundance of HNCO and other nitriles in comets is much less than the X–CN abundance in the ISM ices (up to 10% as proposed by Ehrenfreund *et al.*⁴⁹ towards RAFGL 7009S).

6 Extended sources of molecules

The classical and popular Haser model following which parent molecules are sublimed directly from the nucleus and then decomposed into daughter molecules by photolysis is probably too simplistic. Several pieces of evidence have been brought to show that (i) some molecules thought previously to be parents do not come from the nucleus, but from distributed sources still to be identified and (ii) that some radicals might not come from the decomposition of a parent, but directly from dust grains. The discovery, by the mass spectrometers on Vega and Giotto, that an important fraction of the grains from comet Halley were composed of CHON suggested that these grains are covered by an organic dust mantle, which is in accord with the hypothesis that they could be a source for radicals and various organic molecules.

The problem, however, is far from being settled and no sound evaluation of which part of which molecule is coming from the nucleus or from elsewhere is generally available. One could expect some progress from mapping observations made at the IRAM interferometer at Plateau de Bure (HCN, HNC, CO, H₂CO, H₂S, SO, SO₂...) which are still in the course of reduction.⁶

Icy grains are definite sources of volatiles. Spectral features identified as water ice, at 1.5 and 2.04 μ m, were observed in Hale–Bopp when the comet was at *ca*. 6 AU.⁵⁴ Superheated small icy grains can reach much higher temperatures than the nucleus surface. This could explain the production of water at large heliocentric distances, as well as the changes in production rates and expansion velocities around 3 AU (the distance at which water sublimation from the surface is expected to begin to occur) observed by Biver *et al.*⁵⁵ At 1 AU from the Sun, the lifetime of icy grains is very short, and the volatiles they release are basically indistinguishable from volatiles released from the nucleus, for ground-based observations.

Release from the grain organic mantle has been invoked for the production of CN, CO, C_2 , H_2CO . The organic mantle can be considered as a semi-refractory, intermediate between ices and the mineral refractories. The release mechanisms have, however, never been really clarified. They could be sublimation, pyrolysis or sputtering.

Sublimation of semi-refractories such as small PAHs, or polymers (POM) could easily occur from superheated grains. These large molecules have then to be photodissociated to produce the small molecules and radicals that are observed. This involves a further increase in the parent scale lengths, which may not fit with the source scale lengths advanced for H_2CO or CO (typically 10⁴ km).

Pyrolysis is a mechanism needing higher temperatures which may only be reached in superheated grains of very small size. This destructive mechanism could produce CO or radicals such as CN, but it would be difficult to produce more complex molecules such as H_2CO . Greenberg and Li⁵⁶ have made quantitative evaluations to try to explain the extended source of CO observed by Giotto in comet Halley.⁵⁷ They conclude that even

with extreme assumptions on the grain density and composition, an amount of small grains much larger than observed in P/Halley is necessary to explain the amount of CO released in the extended source.

Sputtering on the grain surface occurs from bombardment of energetic particles. Owing to the small flux of energetic particles available, this is a highly inefficient mechanism which cannot explain the large production rates observed for CO and H_2CO .

In addition, there is also the possibility that, in the inner part of the coma, molecules recondense to form van der Waals molecules and clusters, which dissociate only later, thus mimicking distributed sources. There is not yet any observational basis for such phenomena which are only studied theoretically (*e.g.* ref. 78).

In our opinion, except for H₂CO and for the release from icy grains (but this matters only at large heliocentric distances, see above) the reality of the extended source of volatiles may be questioned. See Section 3 for the discussion on C₂ origin. The case for CO has been discussed by Crifo and Rodionov⁵⁸ who claimed that the extended source observed by Giotto along its path across the coma of P/Halley could be just an artefact due to anisotropic outgassing. A stronger case is perhaps that of CN, for which A'Hearn et al.,40 from broad band spectrophotometric observations, stated that 'we provide strong evidence that most \overline{CN} . . . (is) produced from grains in the coma rather than from nuclear ices'. Indeed, radio observations of several comets have demonstrated that HCN is a major constituent coming from cometary nuclei.⁵⁹ Rauer et al.⁶⁰ have even claimed that all CN comes from HCN, but this pertained to observations of comet Hale-Bopp at large heliocentric distances, where grains are cold, and less likely to release their semi-refractory material. Whether or not HCN (plus other cyanides recently identified, such as HNC, HCCCN and CH₃CN) can numerically account for all the CN radicals observed in the visible cometary spectra is still an open question. Its answer can only come from the comparison of production rates of CN and HCN obtained in a consistent way, taking into account molecular scale lengths and their dependence upon heliocentric distances and solar activity as well as the ejection velocity of photofragments: these parameters are far from being confidently known.

7 Ortho-to-para ratio of water and of other species

Molecules with hydrogen atoms at symmetrical positions may exist in different nuclear spin species, according to the relative orientations of the spins of their hydrogen atoms. Such species are called *ortho* or *para* for molecules with two H atoms such as H_2 , H_2O or H_2CO ; A or E for molecules with three H atoms such as NH_3 or CH_3OH ; A, E or F for molecules with four H atoms such as CH_4 , and so on. Conversions between different spin species, either radiatively or by collisions, are strictly forbidden by quantum mechanics, at least in the gas phase, and are presumably very slow in the solid phase, where they might occur through proton-exchange mechanisms. Therefore, the *ortho*-to-*para* ratio (OPR) or E-to-A ratio of the molecules may be preserved since their formation and may be characteristic of the formation conditions of the molecule, and especially of its temperature (this topic was discussed for cometary water by Crovisier⁶¹ and Mumma *et al.*⁶²).

Fig. 1 shows the OPR (or *E*-to-*A*) ratios, for different molecules of cometary interest, as a function of their equilibrium temperature. For increasing temperatures, the OPR rapidly tends to the statistical weight equilibrium ratio. It is thus only useful for probing very cold temperatures, except for the H_2 molecule, but this molecule is not observed in comets. The figure shows a first group of molecules (H_2O , NH_3 , CH_4) to be more sensitive than another group (H_2S , H_2CO , CH_3OH).

Attempts have been made to determine the OPR of water from IR observations of its v_3 band with the Kuiper Airborne Observatory in comets 1/P Halley and C/1986 P1

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Fig. 1 The *ortho*-to-*para* and *E*-to-*A* population ratios for a selection of molecules with identical H atoms as a function of equilibrium temperature. The ratios have been normalized to their limits for high temperatures.

(Wilson):^{2,63} OPR = 2.5, corresponding to T = 24 K, was found for 1P/Halley whereas OPR = 3 was found for comet Wilson (corresponding to the high-temperature limit). However, the reliability of these results was questioned in ref. 64, because the KAO observations only sampled a selection of ro-vibrational transitions and no correction was made for optical depth effects.

From the high-resolution spectrum of the whole v_3 band of comet Hale–Bopp observed with ISO,¹⁷ an OPR value of 2.45 \pm 0.10 was determined (taking into account optical depth effects). This corresponds to an equilibrium temperature of 25 K.

An OPR ratio of 1.5 ± 0.3 (which would correspond to T = 10 K) was derived from the observation of radio lines of H₂CO in comet Hale–Bopp.⁶⁵ However, this determination, which relies on separate observations of two rotational lines only, could be subject to calibration uncertainties as well as to modelling issues.

From high-resolution ground-based IR observations of CH_4 in comet Hyakutake, Weaver *et al.*⁶⁶ determined the *A*-to-*F* ratio to be indistinguishable from the hightemperature limit and put a lower limit of 50 K on the equilibrium temperature. However, they pointed out that laboratory measurements⁶⁷ indicate that methane could re-equilibrate in the condensed phase over timescales of only hours.

There is, potentially, other information on the spin temperatures of other molecules observed in comets Hyakutake and Hale–Bopp:

In the inversion lines of NH_3 measured by Bird *et al.*;⁵ although the signal-to-noise ratio might be insufficient for a significant determination (ref. 5 and T. Wilson, personal communication);

In the radio lines of methanol; in many cases, several E and A lines were observed simultaneously with the same telescope and spectrometer;

In the ro-vibrational lines of C_2H_2 and $C_2\dot{H_6}$ observed at high resolution with IRTF/CSHELL.

However, if the low spin temperatures indicated by the observations of water in comets Halley and Hale–Bopp are confirmed, one can wonder what is the meaning of these temperatures. Are they the temperature at the formation of the water molecules, as was first speculated?^{61,62} Even if cometary water was formed in cold clouds, chemical

reactions leading to its formation are exothermic reactions, presumably yielding hot water. Or could water re-equilibrate at the temperature of the inner comet nucleus during its long-term storage? In this case, the spin temperature would give us further precious information, but of a quite different nature. Unfortunately, no information is available on the OPR of interstellar water: ro-vibrational lines observed by ISO in several objects were observed in absorption and are heavily saturated; rotational lines also are optically thick (*e.g.* ref. 68 and 69).

Obviously, one needs some information on the *ortho*-to-*para* conversion rates in the conditions pertaining to cometary nucleus ices.

8 HCN–HNC isomers

HNC (hydrogen isocyanide) is an isomeric form of hydrogen cyanide HCN. The energy difference and the potential barrier are such that HCN just does not exist under usual laboratory conditions ($[HNC]/[HCN] = 10^{-15}$ at thermal equilibrium at room temperature). However, HNC is an abundant interstellar molecule with [HNC]/[HCN] as large as 1 in some clouds. It is believed that HCN and HNC are formed in the interstellar medium from the dissociative recombination of HCNH⁺, which produces both isomeric forms with equal yields.

HNC was discovered in comet Hyakutake.⁷ As a first approximation, a comparison of the abundances of HCN and HNC is straightforward, because the corresponding lines of the two species can be observed nearly simultaneously with the same instrumentation (a correction for saturation of the HCN lines may, however, have to be applied). It was found that [HNC]/[HCN] = 0.06, assuming that both species from the nucleus. This high ratio was interpreted as a sign that cometary material may have been formed from unprocessed interstellar matter.

To our surprise, the observations of Hale–Bopp conducted at several radio telescopes^{55,70,71} revealed an [HNC]/[HCN] ratio increasing progressively from 0.03 to ca. 0.20, as the comet approached the Sun. This result is quite unexpected from well mixed HCN and HNC in cometary ices. In comets Hyakutake and Hale–Bopp, the HCN column densities were so large that the analysis had to take into account optical depth effects in the radio lines. An underestimation of these effects might be responsible for the [HNC]/[HCN] variations, although this does not seem to be likely because there is agreement between observations of different lines at different telescopes.

Could HNC be formed from HCN or other species in the inner cometary atmosphere, by reactions similar to those occurring in the interstellar medium, which could depend upon the heliocentric distance? Indeed, due to the very low density pertaining in cometary atmospheres, chemistry in this medium is dominated by destructive photolytic reactions. Ion-neutral reactions can have high rates, but the resulting products can only be minor because of the small ionization fraction of the inner coma. However, as the comet approaches the Sun, the coma temperature, the density and the photolytic rates are increasing, all factors contributing to a higher rate of chemical processing in the coma.

According to a hydrodynamical-chemical model of Rogers and Charnley,⁷² HNC could be formed in cometary atmospheres by collisions of HCN with fast H atoms (the importance of fast hydrogen, coming from water photodissociation, in cometary chemistry was advocated by Roessler⁷³), but another efficient mechanism is a charge-exchange reaction with H_3O^+ , creating HCNH⁺, which then leads to HCN or HNC through charge exchange with NH₃ or CH₃OH. The calculations showed that, for a medium comet such as Hyakutake, [HNC]/[HCN] = 2% at most can be formed, smaller than the ratio observed in this comet. For a highly productive comet such as Hale–Bopp at perihelion, up to [HNC]/[HCN] = 20% could be formed. So, this modelling can

explain the increase of [HNC]/[HCN] in Hale–Bopp when the comet approached the Sun, but it suggests that the largest part of the HNC observed in Hyakutake was of primitive origin.

Such a model is still coarse: it relies on uncertain reaction rates and on preliminary cometary parameters. Furthermore, one should remark that, if HNC is indeed a secondary product, then the published HNC production rates, which were derived assuming a parent molecule distribution, were underestimated. (It was assumed that the conversion from observed column densities to molecular production rates proceeds in the same way for HNC and HCN.)

Since the original nature of HNC seems to be likely, at least in part, it would be interesting to study under what conditions HNC can be preserved in the solid phase, and how they compare with the physical conditions of cometary nuclei. On the other hand, since the possibility of synthesis of minor species in a large comet such as Hale–Bopp seems to be demonstrated, one could wonder if some of the minor species observed with very small abundances in this comet (Table 1) are primary or secondary products.

9 The sodium tail

The observation of a neutral sodium tail by Cremonese *et al.*⁷⁴ was one of the spectacular outcomes of the Hale–Bopp campaign. Sodium is the cometary species which has, by far, the largest fluorescence rate ($g = 15 \text{ s}^{-1}$ at 1 AU from the Sun; a radical like CN has only $g = 0.1 \text{ s}^{-1}$). It thus undergoes a very strong acceleration of 0.22 m s⁻² and forms a linear tail which appears distinct from the already well known dust tail (formed by a much smaller acceleration of dust grains by radiation pressure) and ion tail (formed by interaction of cometary ions with the solar wind). The observed velocities along the Na tail are in very good agreement with those predicted by the acceleration mechanism.

The Na tail is observed to extend over at least 50×10^6 km. This is not compatible with the lifetime of Na against photoionization, as estimated from laboratory measurements. This lifetime (*ca*. 6.2×10^4 s) is used in current models of Na in the exospheres of various solar system objects (Mercury, the Moon, Io). In their analysis of the Na photo-ionization rate, Huebner *et al.*³³ conclude that discrepant values emerge from laboratory cross-sections (6.2×10^4 s) and from theoretical cross-sections (1.7×10^5 s). The analysis of the Hale–Bopp Na tail favours the second one.⁷⁴ Why the 'experimental' cross-sections appear to be inadequate is still to be understood (cf. ref. 75).

The origin of neutral cometary sodium atoms in cometary atmospheres is still not well understood. In addition to this Na tail, a second source of sodium appears to be present in the dust tail. A relative production rate $Q[Na]/Q[H_2O]$ of 5×10^{-6} has been evaluated in the Na tail of comet Hale–Bopp,⁷³ which is much less than the [Na]/[O] cosmic abundance ratio of 2.4×10^{-3} . This means that only a small fraction of cometary sodium is released. Arpigny *et al.*⁷⁶ have argued, from comparison of the kinematics of sodium atoms and of ions in the coma, that sodium is not released by ions, nor directly from the nucleus. Sputtering by high-energy irradiation of cometary dust particles, which is the mechanism invoked for the release of sodium from Mercury and from the Moon, is a highly inefficient mechanism³¹ which cannot explain the observed production of cometary Na. Metallic sodium could sublime from superheated cometary grains, but it seems unlikely that metallic sodium exists freely in grains. The last possibility is that Na comes from the photodissociation of parent molecules released from the nucleus or from dust. With production rates as low as 5×10^{-6} that of water, such molecules will be very difficult to identify. Radio observations are very sensitive to putative Na-parent molecules such as NaOH and NaCl, which are linear molecules with strong dipolar moments. Low upper limits have been obtained for these molecules (ref. 8 and personal communication) but these limits are just of the order of magnitude of the Na production rates, so these radio observations are inconclusive.

10 Conclusion

The exploitation of the observations of comets Hyakutake and Hale–Bopp is only beginning. It was a challenge to write this paper at a moment (end of 1997) when the data on these two comets and their analyses are only very partly available. It may be anticipated that several of the ideas developed in the preceding sections will have to be amended or even discarded on the basis of more complete studies. However, cometary science is of a multidisciplinary nature and can only progress after several iterations confronting facts from very varied origins.

At least 24 constituents of cometary ices have now been identified and preliminary values for their abundances have been proposed. The establishment of more definitive values will necessitate case-by-case studies. In many cases, however, the necessary molecular data (photolytic rates, band strengths, branching ratios between different channels *etc.*) are lacking. As could be expected, the worse situations are found for the most complex molecules or unstable molecules not well known in the laboratory. However, there are also problems for simple molecules such as SO or SO₂.

There are still problems (old and new ones) and controversies about the possible existence of distributed sources of molecules. Icy grains have been directly or indirectly identified and are, plausibly, important sources of volatiles, at least at large heliocentric distances. The organic mantle of grains is potentially an important source of various molecules and radicals, but the mechanisms that could efficiently release these products are still mysterious. An important new fact is the possibility, exemplified by the observation of an [HNC]/[HCN] ratio increasing with gas production rate, of the synthesis of stable neutral molecules in the coma by chemical processes. Up to now, such a process was postulated to be very marginal, or possible only for ionic species. We, thus, can wonder to what extent complex species, observed in small amounts when comet Hale–Bopp was at its peak production rate, are really coming from nuclear ices, or were synthesized in the coma.

Finally, we can wonder how representative of other comets are Hyakutake and Hale–Bopp. These two comets presumably come from the Oort cloud and were formed in the Jupiter–Neptune region, according to current cometary formation theories. Short-period, Jupiter-family comets which come from the Edgeworth–Kuiper belt, in the trans-Neptunian region, might have different compositions and properties. Unfortunately, these Jupiter-family comets are weak objects that are not so well known. This gap in our knowledge could, however, be filled in the future with the cometary space missions such as Rosetta, which will be aimed at these short-period comets.

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Paper 8/00079D; Received 2nd January, 1998