REMOTE OBSERVATIONS OF THE COMPOSITION OF COMETARY VOLATILES

J. CROVISIER and D. BOCKELÉE-MORVAN
Observatoire de Paris-Meudon, F-92195 Meudon, France

Abstract. The volatile species released in the coma are an important clue to the composition of the cometary nucleus ices. Their identification and the measurement of their abundances is possible by remote sensing. Considerable progresses have been made recently using radio and infrared spectroscopy, especially with the observations of the two exceptional comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp).) 24 molecules likely to be parent molecules outgassed from the nucleus have now been identified. Significant upper limits exist for many other species, and the presence of unidentified lines suggests that further species are to be identified. In addition, isotopic varieties have been observed for hydrogen, carbon, nitrogen and sulphur. We will review these results with a special emphasis on the reliability of the identifications and of the molecular production rate determinations. A critical point is to assess whether a given species is a genuine parent molecule outgassed from nuclear ices, or is a secondary product coming from grains or from gas-phase photochemistry. Ground-based spectral imaging, such as radio interferometry, may help resolving this problem.

Keywords: comet, composition, ice, molecule, spectroscopy

1. Introduction

A fundamental goal of cometary science is to determine the composition of comet nucleus ices. In the absence of a direct analysis of this material, one has to analyze the cometary atmosphere formed by volatiles outgassed from the nucleus. This can be done in several steps:

- the identification of molecules present in the coma;
- the determination of their abundances;
- the determination of their origin;
- the determination of the abundance of volatiles in nucleus ices.

We will discuss here how this can be achieved by remote sensing, using ultraviolet, visible, infrared or radio spectroscopy. A complementary method is in situ analysis of the gas by mass spectroscopy — which up to now has only been performed during the space exploration of comet Halley; it is discussed elsewhere in the proceedings of this workshop (Altwegg *et al.*, 1999; see also Eberhardt, 1999).

We have entered a new era where "parent" molecules can now be directly observed, thanks to new techniques such as radio and infrared spectroscopy. Spectacular results have been recently obtained during the apparitions of the exceptional

Composition and Origin of Cometary Materials 1–14, 1999.

TABLE I
Parent molecules in comets: the chronology of first detections.

Year	comet technique	molecules	references [a]
1973	C/1973 E1 (Kohoutek)		
	radio	HCN?	[1]
1976	C/1975 V1 (West)		
	UV	CO (also CS)	[2] [3]
1983	C/1983 H1 (IRAS-Araki-Alcock)		
	radio	NH_3?	[4]
	UV	S_2	[5]
1985–86	1P/Halley		
	radio	HCN, H_2CO?	[6] [7] [8] [9]
	IR	H_2O, CO_2	[10] [11]
1990	C/1989 X1 (Austin), C/1990 K1 (Levy)		
	radio	H_2CO, H_2S, CH_3OH	[12] [13]
1996	C/1996 B2 (Hyakutake)		
	radio	NH_3, HNC, CH_3CN,	[14] [15] [16]
		OCS? HNCO?	[17] [18]
	IR	CH_4, C_2H_2, C_2H_6	[19] [20]
1997	C/1995 O1 (Hale-Bopp)		
	radio	OCS, HNCO, HC_3N, SO_2, HCOOH,	
		H_2CS, NH_2CHO, $HCOOCH_3$ (also SO)	[21] [22] [23]

[a] References: [1] Huebner *et al.* 1974; [2] Feldman and Brune 1976; [3] Smith *et al.* 1980; [4] Altenhoff *et al.* 1983; [5] A'Hearn *et al.* 1983; [6] Despois *et al.* 1986; [7] Schloerb *et al.* 1986; [8] Winnberg *et al.* 1987; [9] Snyder *et al.*, 1989; [10] Mumma *et al.*, 1986; [11] Combes *et al.*, 1986; [12] Bockelée-Morvan *et al.* 1991; [13] Colom *et al.*, 1992; [14] Palmer *et al.*, 1996; [15] Irvine *et al.*, 1996; [16] Dutrey *et al.*, 1996; [17] Woodney *et al.* 1997a; [18] Lis *et al.*, 1997; [19] Mumma *et al.* 1996; [20] Brooke *et al.*, 1996; [21] Lis *et al.*, 1998; [22] Bockelée-Morvan *et al.* 1998b; [23] Woodney *et al.*, 1998.

comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp): the number of identified parent molecules was multiplied by a factor of almost three. A summary of the chronology of the discovery of "parent" molecules in comets is given in Table I. Our state-of-the-art knowledge of the composition of cometary volatiles is summarized in Table II. Other reviews on this topic were recently given by Bockelée-Morvan (1997), Bockelée-Morvan and Crovisier (1998), Crovisier (1998b), Despois (1998), Eberhardt (1998, 1999), Irvine *et al.* (2000), Mumma (1997), Rauer (1999).

2. Identification of Molecular Species

Since the first observation of a cometary spectrum (which was made visually by Donati (1864) in comet Tempel 1864 II), cometary spectroscopy and laboratory molecular spectroscopy have been intimately linked. At that time, the cometary spectral features were not identified. Nowadays, although considerable progresses have been made, many features in cometary spectra are still unidentified.

A high spectral resolution is of a great help for identification: this is possible for rotationally resolved spectra in the radio and (more recently) infrared domains (Crovisier 1998a; Despois 1998).

2.1. The reliability of identifications/detections

To be reliable, the identification or detection of a cometary line should comply with different criteria:

– a good signal-to-noise ratio is required;
– the radio lines should have their shapes and central velocities consistent with those observed for other cometary lines;
– several lines should be observed for confirmation (or the same line should be confirmed in several comets);
– the relative intensities of the observed lines should be in reasonable agreement with predictive models.

These criteria are fulfilled for most of the species listed in Tables I and II. Exceptions are $HCOOCH_3$ and H_2CS which were observed by a single line in a single comet (Bockelée-Morvan *et al.*, 1998b; Woodney *et al.* 1998).

2.2. Unidentified lines

There are still many unidentified lines in cometary spectra, suggesting that we may expect further molecular discoveries, and showing that presently available molecular data are still insufficient for the interpretation of these spectra.

In the visible, detailed spectral surveys show a host of unidentified lines (Arpigny 1995; Brown *et al.*, 1996; Morrison *et al.* 1997; Wyckoff *et al.*, 1999). They are presumably due to radicals and/or ions, for which laboratory spectral data are needed. Progresses in the knowledge of the spectrum of the NH_2 radical recently resulted in the identification of many features in the red region of cometary spectra (Huet *et al.*, 1996).

In the infrared, many unidentified lines have been spotted from the IRTF/-CSHELL high-resolution spectra of comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) (e.g., Magee-Sauer *et al.*, 1998). They might be due to radicals, since the infrared spectra of simple, stable molecules are well known.

A few unidentified lines have also been noted in the radio domain, but they are observed with a limited signal-to-noise ratio.

2.3. Unidentified bands

The 3.4 μm emission band is known since the 1986 observations of comet Halley. Methanol was soon recognized to be a major contributor to this emission (see Bockelée-Morvan *et al.* 1995 and references therein). Several minor constituents recently identified among those listed in Table II (such as some hydrocarbons and HCOOH) are also contributing. It is highly likely that further species are contributing. Progresses on their identification will need a good model of the methanol infrared fluorescence spectrum (there is yet no descriptive model of the relevant infrared bands of methanol), let alone other species. Unfortunately, this spectral region could not be well observed in comet Hale-Bopp because of the very strong dust continuum.

The presence of PAH's in comets is still an open issue. The identification of phenanthrene was claimed from the near-UV spectra of comet Halley observed by the TKS instrument on the Vega probes (Moreels *et al.*, 1993). This identification may be questioned, since it was not confirmed in any other comet, and it relies on rather low-resolution spectra. Admittedly, the TKS observations sampled a region quite close to the nucleus of comet Halley, but this was also the case for the ground-based observations of comet Hyakutake (e.g., Meier *et al.*, 1998c) which passed close to the Earth. The 3.28 μm emission band, characteristic of aromatics, has definitely been seen, but only in a few comets (see the review by Bockelée-Morvan *et al.*, 1995) and not in comet Hale-Bopp. The ISO spectra of comet Hale-Bopp (Crovisier *et al.* 1997) do not show any of the PAH bands which are so ubiquitous in the interstellar medium. However, the comet was only observed by ISO at $r_h >$ 2.9 AU, where PAH's might have not sublimed.

3. From Line or Band Intensities to Column Densities

The fundamental mechanism governing emission by cometary molecules is fluorescence excited by the Sun radiation field. In the inner coma (collisional region), collisions affect the rotational distribution of molecules. This distribution is basically out of equilibrium, between *thermal* and *fluorescence* equilibrium.

To convert *whole band* intensities observed in the infrared, visible or ultraviolet into column densities is rather straightforward: in principle, only the band fluorescence rate (the so-called g-factor) is needed. In most cases, band resonant fluorescence occurs in first approximation (especially for the fundamental bands of vibration in the infrared) and the g-factor can be readily evaluated from the band strength and the solar spectrum. In other cases, the more complex fluorescence cascade must be worked out (e.g., for hot bands of water).

For interpreting single rotational lines (radio) or ro-vibrational lines (infrared), the rotational distribution of the molecule must be known, This requires additional information. It may be provided from the observation of several lines of the

TABLE II

Molecular abundances observed in comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) at $r_h \approx 1$ AU.

Molecule	a)	b)	C/1996 B2		C/1995 O1		remark
H_2O	IR	5	100	[1]	100	[2] [3]	
CO	R IR UV	> 5	6–30	[1] [4] [5]	20	[2] [6] [7]	extended[c)]
CO_2	IR	2			20[d)]	[8]	
CH_4	IR	–	0.7	[1]	0.6	[2]	
C_2H_2	IR	–	≈ 0.5	[9]	0.1	[2]	
C_2H_6	IR	–	0.4	[1]	0.3	[2]	
CH_3OH	R IR	> 5	2	[4]	2	[6] [10]	
H_2CO	R IR	4	0.2–1	[4]	1	[6]	extended[e)]
HCOOH	R	–	–		0.06	[11]	
$HCOOCH_3$	R	–	–		0.06	[11]	
NH_3	R IR	1?	0.5	[12]	0.7	[13] [14]	
HCN	R IR	> 5	0.1	[4]	0.25	[2] [6]	
HNCO	R	–	0.07	[4]	0.06	[10] [11]	
HNC	R	–	0.01	[4] [15]	0.04	[6] [16]	extended
CH_3CN	R	–	0.01	[17]	0.02	[6]	
HC_3N	R	–	–		0.02	[10] [11]	
NH_2CHO	R	–	–		0.01	[10] [11]	
H_2S	R	5	0.8	[17]	1.5	[6]	
OCS	R IR	–	0.1	[18]	0.3	[10] [19]	extended?
SO	R	–	–		0.2–0.8	[10] [11] [20]	extended
CS_2	(R) (UV)	> 5	0.1	[17]	0.2	[6]	from CS[f)]
SO_2	R	–	–		0.1	[11] [20]	
H_2CS	R	–	–		0.02	[21]	
S_2	UV	1	0.005	[5]	–		

a) technique of observation (R: radio);
b) number of detections in other comets;
c) abundance given for *nuclear* + *extended* source;
d) measured at r_h = 2.9 AU;
e) abundance given for *extended* source;
f) CS_2 abundance has been inferred from its presumed daughter CS.

References:
[1] Mumma *et al.*, 1996; [2] Weaver *et al.*, 1998; [3] Dello Russo *et al.*, 1999; [4] Lis *et al.*, 1997; [5] Weaver *et al.*, 1996; [6] Biver *et al.*, 1998; [7] DiSanti *et al.*, 1999; [8] Crovisier *et al.*, 1997; [9] Brooke *et al.*, 1996; [10] Lis *et al.*, 1998; [11] Bockelée-Morvan *et al.*, 1998b; [12] Palmer *et al.*, 1996; [13] Bird *et al.*, 1997; [14] Bird *et al.*, 1998; [15] Irvine *et al.*, 1996; [16] Irvine *et al.*, 1998; [17] Bockelée-Morvan 1997; [18] Woodney *et al.*, 1997a; [19] Dello Russo *et al.*, 1998; [20] Kim *et al.*, 1998; [21] Woodney *et al.*, 1997b.

molecule. The radio lines of methanol are particularly suitable for this, since it is often possible to observe several of these lines simultaneously with the same instrumentation (e.g., Biver *et al.*, 1998). Series of ro-vibrational lines have also been observed by ISO or CSHELL/IRTF: for H_2O (Crovisier *et al.*, 1997, 1999; Dello Russo *et al.*, 1999) or CO (DiSanti *et al.*, 1999), HCN, C_2H_2.... But for a single line observation, one has to assume the same rotational temperature as that observed for other species (if possible, at the same moment within a similar field of view).

Another approach is theoretical modelling of rotational excitation. One has to solve for the evolution between thermal equilibrium and fluorescence equilibrium. The kinetic temperature of the gas and its evolution with distance to nucleus must be known, as well as the collisional cross sections (which are in fact very poorly known).

Optical depth effects may be a problem, but only for abundant species (e.g., H_2O) or in productive comets (e.g., HCN radio lines in comet Hale-Bopp).

4. From Column Densities to Molecular Production Rates

In order to convert column densities into molecular production rates, the knowledge of the density distribution is needed. This is intimately linked to the problem of the origin of the molecules:

- molecule directly sublimed from the nucleus;
- daughter species coming from the photodissociation of a parent;
- molecule coming from a "distributed source" such as dust, or synthesized by chemical reactions in the coma, or produced by still unknown mechanisms.

The simplistic Haser or vectorial models are popularly used in this context. They require the knowledge of the molecular velocities (which can be inferred from radio line shapes) and photodissociation rates (which can be evaluated from laboratory data and the solar spectrum). There is still a need for laboratory data on photodissociation rates. Some of them are just unknown; this is the case for most radicals, but also for the recently discovered species H_2CS, $HCOOCH_3$ and NH_2CHO. It must be noted that those for SO and SO_2 are still debated (discrepant values are reported in the literature; Kim *et al.*, 1998).

Spherical symmetry, which is a fundamental hypothesis in these models, is broken in real cases because of anisotropic outgassing. The resulting errors on production rate evaluations from observations averaged over wide circular fields of view are not very large (typically 10–20% for realistic cases; Biver *et al.*, in preparation). Much more severe could be the errors resulting from the assumption of a parent distribution when the molecule is indeed coming from a distributed source.

The direct mapping of "parent" molecules is now possible. At radio wavelengths, successful observations with spatial resolution of the order of the arcsecond could be made with the BIMA, OVRO and IRAM Plateau-de-Bure interferometers (Wink *et al.*, 1998; Despois 1998 and references therein); with larger fields of view and coarser spatial resolution, "on-the-fly" mapping and multibeam receivers were used (Lovell *et al.*, 1998; Womack *et al.* 1998). In the infrared, long-slit spectral observations with CSHELL/IRTF could study the extension of molecules such as CO and OCS. Such observations are of a considerable help for finding a solution to these problems.

CO and H_2CO have manifestly distributed sources. Eberhardt (1998 and references therein) argues that the mass spectrometry observations of Giotto in comet Halley are fully consistent with CO coming from H_2CO (an interesting critical discussion of this interpretation, however, is given by Crifo *et al.*, 1999). This does not seem to be the case for other comets, for which the CO production rate is much larger than that of H_2CO. In comet Hale-Bopp, 1-D spectral imaging with CSHELL/IRTF (DiSanti *et al.*, 1999; Weaver *et al.*, 1998) has definitely shown the existence of a distributed source when $r < 2$ AU. On the other hand, radio interferometric observations of comet Hyakutake around closest approach have directly shown a nuclear source of CO (Bockelée-Morvan *et al.*, in preparation). As a matter of fact, both a nuclear and a distributed source seem to coexist, the latter being turned on only at small heliocentric distances (DiSanti *et al.* 1999). However, the nature of the distributed sources and of possible desorption mechanisms from dust for CO and H_2CO are unknown: there is no quantitative explanation available (Greenberg and Li 1998).

The case for HCN and CN is now well documented. There is no doubt that HCN is a major parent for the CN radical. Indeed, observations of comet Hale-Bopp at $r_h > 2.9$ AU indicate that all CN could come from HCN (Rauer *et al.*, 1997). However, these two species have incompatible spatial distribution and production rates at smaller r_h's (Biver *et al.* in preparation; Festou *et al.* 1998). An additional source for CN seems to be required (HC_3N and CH_3CN have been identified, but their contribution is nominal). A'Hearn *et al.* (1995) have proposed a contribution from dust, but once again, the desorption mechanism problem is not solved.

The role of chemical reactions to synthesize molecules in the coma is now exemplified by HNC. This species was first detected in comet Hyakutake (Irvine *et al.*, 1996). In comet Hale-Bopp the [HNC]/[HCN] ratio was found to increase as the comet approached the Sun (Biver *et al.*, 1997, 1998; Irvine *et al.* 1998). This strongly suggests that a major part of the cometary HNC is produced by chemical reactions (Rogers and Charnley 1998; Irvine *et al.*, 1998). Could other minor species, listed in Table II, be formed in this way?

5. From Gas Molecular Production Rates to Ice Molecular Abundances

Because of the different volatilities of cometary ice components, sublimation fractionation occurs. Further complications are due to the evolution of the outer layers of the nucleus during sublimation–recondensation processes. These problems will not be discussed here (they are the subject of several other papers given at the workshop). As a result, the molecular production rates observed in the gas phase *do not* directly reflect the ice molecular abundances. Important clues to this phenomenon were obtained from the observation of the production rate evolutions in comet Hale-Bopp over $0.9 < r_h < 7$ AU (Biver *et al.*, 1997, 1998; Bockelée-Morvan and Rickman 1998).

6. Results and Discussion

Our present knowledge of volatile abundances is summarized in Table II. This table must be read and used with the cautions explained in the previous sections. The signal-to-noise ratio of the observations is generally not a problem. Most of the uncertainties in the abundance determinations may be attributed to absolute calibration, modelling uncertainties, and the difficulty to evaluate the water production rates to which abundances are usually normalized. Despite these shortcomings, we believe that for most molecules, the overall error is less (but not much less) than a factor of two. The real problem is for species such as CO or H_2CO which are known (or suspected) to have extended sources. Which fraction is coming from the nucleus or from an extended source, and for this latter, what is its scale length, are very ill-known parameters. In such cases, the errors may be large.

The production rate of water, which appears to dominate the composition of cometary ices, is commonly used to normalize cometary volatile abundances. This is a problem, since most of the time $Q[H_2O]$ is ill known: direct observations of water, which have to be performed in the infrared domain, are rare; indirect determinations (e.g., from the OH radical observed in the radio or UV) have to rely on sophisticated modelling.

Several isotopic species have now been directly observed from their radio lines, as can be seen in the summary given in Table III. The detection of HDO and other species are state-of-the-art observations on which the signal-to-noise ratio is limited. For these observations, single lines are observed and the determination of production rates rely on modelling; the problem of the $Q[H_2O]$ evaluation noted above is also critical. The same enriched [D]/[H] ratio ($\approx 3 \times 10^{-4}$) has been observed in comets 1P/Halley (from in situ mass spectroscopy), C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp). As discussed by Bockelée-Morvan *et al.* (1998a) and elsewhere in the proceedings of this workshop, the [D]/[H] ratio is a touchstone for formation scenarios of comets. The three comets for which [D]/[H] was measured are presumed to come from the Oort cloud. This ratio will be difficult to measure by remote sensing in Jupiter-family comets, which are much weaker objects. For carbon, nitrogen, and sulphur which are heavier atomic species less sensitive to fractionation during chemical reactions, the isotopic abundances appear to be cosmic (solar).

TABLE III
Isotopic ratios in comets.

Isotopes Molecule	comet	method [a]	cosmic ratio	comet ratio	ref. [b]
[D]/[H]					
H_3O^+	1P/Halley	M	1.5×10^{-5}	$3.08 \pm 0.53 \times 10^{-4}$	[1]
				$3.02 \pm 0.22 \times 10^{-4}$	[2]
H_2O	C/1996 B2	R		$2.9 \pm 1.0 \times 10^{-4}$	[3]
	C/1995 O1	R		$3.3 \pm 0.8 \times 10^{-4}$	[4]
HCN	C/1995 O1	R		$2.3 \pm 0.4 \times 10^{-3}$	[5]
NH	C/1996 B2	V		$< 6 \times 10^{-3}$	[6]
CH	C/1996 B2	V		$< 3 \times 10^{-2}$	[6]
CH_3OH	1P/Halley	M		$< 1 \times 10^{-2}$	[7] [c]
$[^{18}O]/[^{16}O]$					
H_3O^+	1P/Halley	M	2.0×10^{-3}	$1.93 \pm 0.12 \times 10^{-3}$	[1]
				$2.13 \pm 0.18 \times 10^{-3}$	[2]
$[^{13}C]/[^{12}C]$					
CN	1P/Halley	V	1.1×10^{-2}	$1.05 \pm 0.13 \times 10^{-2}$	[8]
HCN	C/1996 B2	R		$2.9 \pm 1.0 \times 10^{-2}$	[9] [d]
	C/1995 O1	R		$1.11 \pm 0.18 \times 10^{-2}$	[10]
				$0.90 \pm 0.09 \times 10^{-2}$	[11]
$[^{15}N]/[^{14}N]$					
CN	1P/Halley	V	3.6×10^{-3}	$< 3.6 \times 10^{-3}$	[8]
HCN	C/1995 O1	R		$3.1 \pm 0.4 \times 10^{-3}$	[11]
$[^{34}S]/[^{32}S]$					
atomic S	1P/Halley	M	4.2×10^{-2}	$4.5 \pm 1.0 \times 10^{-2}$	[12]
CS	C/1995 O1	R		$3.7 \pm 0.4 \times 10^{-2}$	[11]

[a] M: mass spectroscopy; R: radio; V: visible;
[b] References: [1] Balsiger *et al.*, 1995; [2] Eberhardt *et al.*, 1995; [3] Bockelée-Morvan *et al.*, 1998a; [4] Meier *et al.*, 1998b; [5] Meier *et al.*, 1998a; [6] Meier *et al.*, 1998c; [7] Eberhardt *et al.*, 1994; [8] Kleine *et al.*, 1995; [9] Lis *et al.*, 1997; [10] Lis *et al.*, 1998; [11] Jewitt *et al.*, 1997; [12] Krankowsky *et al.*, 1986;
[c] The ratio listed here is [deuterated CH_3OH]/[CH_3OH] and not [D]/[H];
[d] This ratio is possibly affected by blending of the $H^{13}CN$ line by a SO_2 line.

The ortho-to-para ratio (OPR) of water is supposed to be conserved during radiative or collisional transitions and to keep memory of the state of water at its formation. It can be estimated from high-resolution infrared spectra such as those obtained some time ago from the KAO and recently by ISO. It has yet been measured in four comets: 1P/Halley,C/1986 P1 (Wilson), C/1995 O1 (Hale-Bopp) and 103P/Hartley 2 (Mumma *et al.*, 1993; Crovisier *et al.* 1997, 1999). For three of these comets (the "Oort cloud comets" P/Halley and Hale-Bopp and the Jupiter-family comet P/Hartley 2), the OPR was found to be smaller than 3, corresponding to spin temperatures in the range 25–35 K. The meaning of such cold temperatures is still to be understood. Further results can be expected from other species (CH_4, H_2CO, CH_3OH...).

Is there a variation of composition from comet to comet? The sample of comets for which the abundance of even a limited number of parent molecules is known is still extremely small (Table II). However, there are strong suspicions of variations for species such as CO, CH_3OH or H_2S. An important challenge is to investigate a possible correlation between chemical differences and the dynamical classes of the comets, which could betray their different origins and/or thermal histories. From the observations of radicals in almost a hundred comets, A'Hearn *et al.* (1995) have identified two classes of comets: the first has *typical* abundances while the second is depleted in *carbon-chain* molecules. They suggested that Jupiter-family comets are linked with the latter class. How does this translate into possible differences in the production of parent molecules? Jupiter-family comets seem to be much less productive of CO with [CO]/[H_2O]$\leq$ 1.5% at $r_h \approx 1$ AU (Weaver *et al.*, 1994; Feldman *et al.*, 1997), but the statistics is still very poor, these weaker comets being much harder to observe. On the other hand, Schulz *et al.* (1998) questioned the reality of the two taxonomic classes introduced by A'Hearn *et al.*, by pointing out that a heliocentric distance effect could be the reason for the dichotomy, since *carbon-depleted* comets were rather those observed at large heliocentric distances ($r_h > 1.6$ AU), while *typical* comets were observed at $r_h \approx 1$ AU.

How complete is Table II? We believe it could be complete for major species with abundances relative to water of the order of — let us say — roughly 1%. On the other hand, it is obvious that many more minor species are still to be discovered. Stringent upper limits on many species have been obtained in comets Hyakutake and Hale-Bopp that have not yet been exploited nor reported. There are still elusive molecules such as O_2, N_2 or H_2 which, having no strong spectral signatures, cannot be investigated by remote sensing. N_2 abundances have been derived in the past from the claimed detection of the $B-X$ bands of N_2^+; these bands were not reported in recent high-resolution cometary spectra.

References

A'Hearn M.F., Feldman, P.D. and Schleicher, D.J.: 1983, 'The discovery of S_2 in comet IRAS-Aracki-Alcock 1983d', *Astrophys. J.* **274**, L99–L103.

A'Hearn, M.F., Millis, R.L., Schleicher, D.G., Osip, D.J. and Birch, P.V.: 1995, 'The ensemble properties of comets: results from narrowband photometry of 85 comets, 1976–1992', *Icarus* **118**, 223–270.

Altenhoff, W.J., Batrla, W., Huchtmeier, W.K., Schmidt, W.K., Stumpff, P. and Walmsley, C.M.: 1983, 'Radio observations of comet 1983d', *Astron. Astrophys.* **125**, L19–L22.

Altwegg, K., Balsiger, H. and Geiss, J.: 1999, 'Composition of the volatile material in Halley's coma from in situ measurements', *Space Sci. Rev.*, this volume.

Arpigny, C.: 1995, 'Spectra of comets: ultraviolet and optical regions', in *Laboratory and Astronomical High Resolution Spectra*, ed. A.J. Sauval, R. Blomme and N. Grevesse, ASP Conf. Series Vol. **81**, 362–383.

Balsiger, H., Altwegg, K., Geiss, J.: 1995, 'D/H and $^{18}O/^{16}O$ ratio in the hydronium ion and in neutral water from in situ ion measurements in comet Halley', *J. Geophys. Res.***100**, 5827–5834.

Bird, M.K., Huchtmeier, W.K., Gensheimer, P., Wilson, T.L., Janardhan, P. and Lemme, C.: 1997, 'Radio detection of ammonia in comet Hale-Bopp', *Astron. Astrophys.* **325**, L5–L8.

Bird, M.K., Janardhan, P., Wilson, T.L., Huchtmeier, W.K., Gensheimer, P. and Lemme, C.: 1998, 'K-band radio observations of comet Hale-Bopp: detections of ammonia and (possibly) water', *Earth Moon Planets* (in press).

Biver, N., *et al.*: 1997, 'Evolution of the outgassing of comet Hale-Bopp (C/1995 O1) from radio observations', *Science* **275**, 1915–1918.

Biver, N., *et al.*: 1998, 'Long term evolution of the outgassing of comet Hale-Bopp from radio observations', *Earth Moon Planets* (in press).

Bockelée-Morvan, D., Colom, P., Crovisier, J., Despois, D., Paubert, G.: 1991, 'Microwave detection of hydrogen sulfide and methanol in comet Austin', (1989c$_1$) *Nature* **350**, 318–320.

Bockelée-Morvan, D., Brooke, T.Y. and Crovisier, J.: 1995, 'On the origin of the 3.2- to 3.6-μm emission features in comets', *Icarus* **116**,18-39.

Bockelée-Morvan, D.: 1997, 'Cometary volatiles : The status after comet C/1996 B2 Hyakutake', in *Molecules in Astrophysics: Probes and Processes, IAU Symp. 178*, ed. E.F. van Dishoeck, Kluwer, 219–235.

Bockelée-Morvan, D. and Crovisier, J.: 1998, 'New results on the composition of comets', in *Planetary Systems: the Long View*, IXth Rencontres de Blois, Éditions Frontières, *in press*.

Bockelée-Morvan, D. and Rickman, H.: 1998, 'Gas production curves and their interpretation', *Earth Moon Planets* (in press).

Bockelée-Morvan, D., *et al.*: 1998a, 'Deuterated water in comet C/1996 B2 (Hyakutake) and its implication for the origins of comets', *Icarus* **133**, 147–162.

Bockelée-Morvan D., *et al.*: 1998b, 'A molecular survey of comet C/1995 O1(Hale-Bopp) at the IRAM telescopes', *Earth Moon Planets* (in press).

Brooke, T.Y., Tokunaga, A.T., Weaver, H.A., Crovisier, J., Bockelée-Morvan, D. and Crips, D.: 1996, 'Detection of acetylene in the infrared spectrum of Hyakutake', *Nature* **383**, 606–608.

Brown, M.E., Bouchez, A.H., Spinrad, A.H. and Johns-Krull, C.M.: 1996, 'A high-resolution catalog of cometary emission lines', *Astron. J.* **112**, 1197–1202.

Colom, P., Crovisier, J., Bockelée-Morvan, D., Despois, D. and Paubert, G.: 1992, 'Formaldehyde in comets: I. Microwave observations of P/Brorsen-Metcalf (1989 X), Austin (1990 V) and Levy (1990 XX)', *Astron. Astrophys.* **264**, 270–281.

Combes, M., *et al.*: 1986, 'Infrared sounding of comet Halley from Vega 1', *Nature* **321**, 266–268.

Crifo, J.-F., Rodionov, A.V., Bockelée-Morvan, D.: 1999, 'The dependence of the circumnuclear coma structure on the properties of the nucleus, III. First modelling of a CO-dominated coma, with applications to comets 46P/Wirtanen and P/Schwachmann-Wachmann 1', *Icarus* **138**, 85–106.

Crovisier, J., Leech, K., Bockelée-Morvan, D., Brooke, T.Y., Hanner, M.S., Altieri, B., Keller, H.U. and Lellouch, E.: 1997, 'The spectrum of comet Hale-Bopp (C/1995 O1) observed with the Infrared Space Observatory at 2.9 AU from the Sun', *Science* **275**, 1904–1907.

Crovisier, J.: 1998a, 'Infrared observations of volatile molecules in comet Hale-Bopp', *Earth Moon Planets* (in press).

Crovisier, J.: 1998b, 'Physics and chemistry of comets: recent results from comets Hyakutake and Hale-Bopp; answers to old questions and new enigmas', *Faraday Discuss.* **109**, 437–452.

Crovisier, J., *et al.*: 1999, 'ISO spectroscopic observations of short-period comets', in *The Universe as seen by ISO*, ESA **SP-427** (in press).

Dello Russo, N., DiSanti, M.A., Mumma, M.J., Magee-Sauer, K. and Rettig, T.W.: 1998, 'Carbonyl sulfide in comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp): evidence for an extended source in Hale-Bopp', *Icarus* **135**, 377–388.

Dello Russo, N., Mumma, M.J., DiSanti, M.A., Magee-Sauer, K., Novak, R. and Rettig, T.W.: 1999, 'Water production and release in comet C/1995 O1 Hale-Bopp', *Icarus*, in press.

Despois, D., Crovisier, J., Bockelée-Morvan, D., Schraml, J., Forveille, T. and Gérard, E.: 1986, 'Observations of hydrogen cyanide in comet Halley', *Astron. Astrophys.* **160**, L11–L12.

Despois, D.: 1998, 'Radio line observations of molecular and isotopic species, implications on the interstellar origin of cometary ices', *Earth Moon Planets* (in press).

DiSanti, M.A., Mumma, M.J., Dello Russo, N., Magee-Sauer, K., Novak, R. and Rettig, T.W.: 1999, 'Identification of two sources of carbon monoxide in comet Hale-Bopp, , *Nature* **399**, 662-665.

Donati, G.B.: 1864, 'Schreiben des Herrn Professors Donati', *Astron. Nachrichten* **62**, 375–378.

Dutrey, A., *et al.*: 1996, 'Comet C/1996 B2 (Hyakutake)', *IAUC* No 6364.

Eberhardt, P., Meier, R., Krankowsky, D. and Hodges, R.R.: 1994, 'Methanol and hydrogen sulfide in P/Halley', *Astron. Astrophys.* **288**, 315–329.

Eberhardt, P., Reber, M., Krankowsky, D. and Hodges, R.R.: 1995, 'The D/H and $^{18}O/^{16}O$ ratios in water from comet P/Halley', *Astron. Astrophys.* **302**, 301–316.

Eberhardt, P.: 1998, 'Volatiles, isotopes and origin of comets', in *Asteroids, Comets, Meteors 1996*, COSPAR Colloquium 10 (in press).

Eberhardt, P.: 1999,'Composition of comets: the in situ view', in *Cometary Nuclei in Space and Time, IAU Coll. 168*, ed. M.F. A'Hearn, ASP Conf. Series (in press).

Feldman, P.D. and Brune, W.H.: 1976, 'Carbon production in comet West (1975n)', *Astrophys. J.* **209**, L45–L48.

Feldman, P.D., Festou, M.C., Tozzi, G.P. and Weaver, H.A.: 1997, 'The CO_2/CO abundance ratio in 1P/Halley and several other comets observed by *IUE* and *HST*', *Astrophys. J.* **475**, 829–834.

Festou, M.C., Barale, O., Davidge, T., Stern, S.A., Tozzi, G.P., Womack, M. and Zucconi, J.M.: 1998, 'Tentative identification of the parent of CN radicals in comets: C_2N_2', *BAAS* **30**, 1089.

Greenberg, J.M. and Li, A: 1998, 'From interstellar dust to comets: the extended CO source in comet Halley', *Astron. Astrophys.* **332**, 374–384.

Huebner, W.F., Snyder, L.E. and Buhl, D.: 1974, 'HCN radio emission from comet Kohoutek (1973f)', *Icarus* **23**, 580–585.

Huet, T.R., Hadj Bachir, I., Bolvin, H., Zellagui, A., Destombes, J.L. and Vervloet, M.: 1996, 'NH_2 transitions of cometary interest in the near infrared', *Astron. Astrophys.* **311**, 343–346.

Irvine, W.M., *et al.*: 1996, 'Spectroscopic evidence for interstellar ices in Comet Hyakutake', *Nature* **383**, 418–420.

Irvine, W.M., Bergin, E.A., Dickens, J.E., Jewitt, D., Lovell, A.J., Matthews, H.E., Schloerb, F.P. and Senay, M.: 1998, 'Chemical processing in the coma as the source of cometary HNC', *Nature* **393**, 547-550.

Irvine, W.M., Schloerb, F.P., Crovisier, J., Fegley, B. and Mumma, M.J.: 2000, 'Comets: a link between interstellar and nebular chemistry', in *Protostars and Planets IV*, V. Manning, A. Boss and S. Russell (edts), University of Arizona Press, Tucson (in press).

Jewitt, D.C., Matthews, H.E., Owen, T.C. and Meier, R.: 1997, 'Measurements of $^{12}C/^{13}C$, $^{14}N/^{15}N$, and $^{32}S/^{34}S$ ratios in comet Hale-Bopp', (C/1995 O1) *Science* **278**, 90–93.

Kim, S.J., Bockelée-Morvan, D., Crovisier, J. and Biver, N.: 1998, 'Fluorescence and collisional processes of SO and SO_2 in comet Hale-Bopp', (C/1995 O1) *Earth Moon Planets* (in press).

Kleine, M., Wyckoff, S., Wenhinger, P.A. and Peterson, B.A.: 1995, 'The carbon isotope abundance ratio in comet Halley', *Astrophys. J.* **439**, 1021–1033.

Krankowsky, D., *et al.*: 1986, 'In situ gas and ion composition measurements at Comet Halley', *Nature* **321**, 326–329.

Lis, D.C., Keene, J., Young, K., Phillips, T.G., Bockelée-Morvan, D., Crovisier, J., Schlike, P., Goldsmith, P.F. and Bergin, E.A.: 1997, 'CSO observations of comet C/1996 B2 (Hyakutake)', *Icarus* **130**, 355–372.

Lis, D.C., Mehringer, D., Benford, D., *et al.*: 1998, 'New molecular species in comet c/1995 O1 (Hale-Bopp) observed with the Caltech Submillimeter Observatory', *Earth Moon Planets* (in press).

Lovell, A.J., Schloerb, F.P., Dickens, J.E., De Vries, C.H., Senay, M.C. and Irvine, W.M.: 1998, 'HCO^+ imaging of comet C/Hale-Bopp 1995 O1', *Astrophys. J.* **497**, L117–L120.

Magee-Sauer, K., Mumma, M.J., DiSanti, M.A., Dello Russo, N. and Rettig, T.W.: 1998, 'CSHEL-L observations of HCN, C_2H_2, and NH_3 in comets C/1995 O1 (Hale-Bopp) and C/1996 B2 (Hyakutake)', *BAAS* **30**, 1064.

Meier, R., Owen, T.C., Jewitt, D.C., Matthews, H.E., Senay, M., Biver, N., Bockelée-Morvan, D., Crovisier, J. and Gautier, D.: 1998a, 'Deuterium in comet C/1995 O1 (Hale-Bopp): Detection of DCN', *Science* **279**, 1707–1710.

Meier, R., Owen, T.C., Matthews, H.E., Jewitt, D.C., Bockelée-Morvan, D., Biver, N., Crovisier, J. and Gautier, D.: 1998b, 'A determination of HDO/H_2O in comet C/1995 O1 (Hale-Bopp), *Science* **279**, 842–844.

Meier, R., Wellnitz, D., Kim, S.J. and A'Hearn, M.F.: 1998c 'The NH and CH bands of comet C/1996 B2 (Hyakutake)', *Icarus* **136**, 268–279.

Moreels, J., Clairemidi, J., Hermine, P., Brechignac, P. and Rousselot, P.: 1993, 'Detection of a polycyclic aromatic molecule in P/Halley', *Astron. Astrophys.* **282**, 643–656.

Morrison, N.D., Knauth, D.C., Mullis, C.M. and Lee, W.: 1997, 'High-resolution optical spectra of the head of comet C/1996 B2 (Hyakutake)', *Publ. Astron. Soc. Pacific*, **109**, 676–681.

Mumma, M.J., Weaver, H.A., Larson, H.P., Davis, D.S. and Williams, M.: 1986, 'Detection of water vapor in Halley's comet', *Science* **232**, 1523–1528.

Mumma, M.J., Weissman, P.R. and Stern, S.A.: 1993, 'Comets and the origin of the solar system: Reading the Rosetta stone' in *Protostars and Planets III*, E.H. Levy and J.I. Lunine (edts), University of Arizona Press, Tucson, 1177–1252.

Mumma, M.J., DiSanti, M.A., Dello Russo, N., Fomenkova, M., Magee-Sauer, K., Kaminski, C.D. and Xie, D.X.: 1996, 'Detection of abundant ethane and methane, along with carbon monoxide and water, in comet C/1996 B2 (Hyakutake): evidence for interstellar origin', *Science* **272**, 1310–1314.

Mumma, M.J.: 1997, 'Organic volatiles in comets: their relation to interstellar ices and solar nebula material', in *From Stardust to Planetesimals*, Y.J. Pendleton and A.G.G.M. Tielens eds, ASP Conf. Series **122**, 369–398.

Palmer, P., Wootten, A., Butler, B., Bockelée-Morvan D., Crovisier, J., Despois, D., Yeomans, D.K.: 1996, 'Comet Hyakutake: First secure detection of ammonia in a comet' *BAAS* **28**, 927–928.

Rauer, H., Arpigny, C., Boehnhardt, H., Colas, F., Crovisier, J., Jorda, L., Küppers, M., Manfroid, J., Rembor, K. and Thomas, N.: 1997, 'Optical observations of comet Hale-Bopp (C/1995 O1) at large heliocentric distances before perihelion', *Science* **275**, 1909–1912.

Rauer, H.: 1999, 'Remote observations of cometary volatiles and implications on comet nuclei', in *Cometary Nuclei in Space and Time, IAU Coll. 168*, ed. M.F. A'Hearn, ASP Conf. Series (in press).

Rodgers, S.D. & Charnley, S.B.: 1998, 'HNC and HCN in comets', *Astrophys. J.* **501**, L227–L230.

Schloerb, F.P., Kinzel, W.M., Swade, D.A. and Irvine, W.M.: 1986, 'HCN production rates from comet Halley', *Astrophys. J.* **310**, L55–L60.

Schulz, R., Arpigny, C., Manfroid, J., Stüwe, J.A., Tozzi, G.P., Rembor, K., Cremonese, G. and Peschke, S.: 1998, 'Spectral evolution of ROSETTA target comet 46P/Wirtanen', *Astron. Astrophys.* **335**, L46–L49.

Smith, A.M., Stecher, T.P. and Casswell, L.: 1980, 'Production of carbon, sulphur, and CS in comet West', *Astrophys. J.* **242**, 402–410.

Snyder, L.E., Palmer, P. and de Pater, I.: 1989, 'Radio detection of formaldehyde emission from comet Halley', *Astron. J.* **97**, 246–253.

Weaver, H.A., Feldman, P.D., McPhate, J.B., A'Hearn, M.F., Arpigny, C. and Smith, T.E.: 1994, 'Detection of CO Cameron band emission in comet P/Hartley 2 (1991 XV with the *Hubble Space Telescope*', *Astrophys. J.* **422**, 374–380.

Weaver, H.A., Feldman, P.D., McPhate, J.B., A'Hearn, M.F., Arpigny, C., Brandt, J.C. and Randall, C.E.: 1996, 'Ultraviolet spectroscopy and optical imaging of comet Hyakutake (1996 B2) with HST', in *Asteroids, Comets, Meteors 1996*, COSPAR Colloquium 10 (book of abstracts).

Weaver, H.A., Brooke, T.Y., Chin, G., Kim, S.J., Bockelée-Morvan, D. and Davies, J.K.: 1998, 'Infrared spectroscopy of comet Hale-Bopp', *Earth Moon Planets* (in press).

Wink, J., *et al.*: 1998, 'Evidences for extended sources and temporal modulations in molecular observations of C/1995 O1(Hale-Bopp) at IRAM interferometer', *Earth Moon Planets* (in press).

Winnberg, A., Ekelund, L. and Ekelund, A.: 1987, 'Detection of HCN in comet P/Halley', *Astron. Astrophys.* **172**, 335–341.

Womack, M. Homoch, A., Festou, M.C., Mangum, J., Uhl, W.T. and Stern, S.A.: 1998, 'Maps of HCO^+ emission in C/1995 O1 (Hale-Bopp',) *Earth Moon Planets* (in press).

Woodney, L.M., McMullin, J. and A'Hearn,M.F.: 1997a, 'Detection of OCS in comet Hyakutake (C/1996 B2)', *Planet. Space Sci.* **45**, 717–719.

Woodney, L.M., McMullin, J., A'Hearn,M.F. and Samarasinha, N.: 1997b, *IAU Circ.* 6607

Woodney, L.M., A'Hearn, M.F., Lisse, C., McMullin, J. and Samarasinha, N.: 1998, 'Sulfur chemistry at millimeter wavelengths in C/Hale-Bopp', *Earth Moon Planets* (in press).

Wyckoff, S., Heyd, R.S. and Fox, R.: 1999, 'Unidentified molecular bands in the plasma tail of comet Hyakutake (C/1996 B2)', *Astrophys. J.* **512**, L73–L76.

Address for correspondence: Jacques Crovisier, Observatoire de Paris-Meudon, F-92195 Meudon, France (crovisie@obspm.fr)