Astronomy & Astrophysics manuscript no. upper'lim'rev February 13, 2004
(DOI: will be inserted by hand later)

The composition of ices in comet C/1995 O1 (Hale-Bopp) from radio spectroscopy:

Further results and upper limits on undetected species

J. Crovisier[1], D. Bockelée-Morvan[1], P. Colom[1], N. Biver[1], D. Despois[2], D.C. Lis[3], and the Team for target-of-opportunity radio observations of comets

[1] Observatoire de Paris, F-92195, Meudon, France e-mail: jacques.crovisier@obspm.fr
[2] Observatoire de Bordeaux, B.P. 89, F-33270, Floirac, France
[3] California Institute of Technology, MS 320-47, Pasadena, CA 91125, USA

Received 14 November 2003 / Accepted 26 January 2004

Abstract. From radio spectroscopic observations of comets, more than 22 molecules, radicals and ions, plus several isotopologues, were detected, the majority of them being recently revealed in comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp). Among them, 6 molecules were detected for the first time (Bockelée-Morvan et al. 2000) in the course of a spectral survey conducted at radio wavelengths in comet Hale-Bopp with the CSO, the IRAM 30-m telescope and Plateau de Bure interferometer. In addition, many species were searched for unsuccessfully, some of them with stringent upper limits. We present here a review of these observations and further analysis of their results. This include: (i) confirmed detection of acetaldehyde (CH_3CHO); (ii) limits on small molecules such as ketene (H_2CCO) or methanimine (CH_2NH); (iii) limits on the abundance ratios in homologous series such as HC_5N/HC_3N, ethanol/methanol, acetic acid/formic acid; (iv) searches for precursors of key cometary species such as atomic Na and HNC; (v) constraints on more exotic species ranging from water dimer $(H_2O)_2$ to glycine; (vi) detection of the $H_2^{34}S$ isotopic species and independent observations of HDO and DCN; (vii) limits on several other deuterated species; (viii) limits on several radicals and ions and a tentative detection of the C_2H radical; (ix) the presence of unidentified lines. Typical abundance upper limits of 2–5 $\times 10^{-4}$ relative to water are achieved for many species. Better upper limits are obtained for some linear molecules with high dipole moments. But really complex molecules such as dimethyl ether or glycine are poorly constrained. These results should give important clues to the chemical composition of cometary ices, to the formation mechanisms of cometary material, and to the chemical processes which occur in the inner coma.

Key words. astrochemistry – comets: general – comets: individuals: C/1995 O1 (Hale-Bopp) – line: identification – radio lines: solar system – solar system: formation

1. Introduction

From radio spectroscopic observations of comets, more than 22 molecules, radicals and ions, plus several isotopologues, were detected, the majority of them being recently revealed in comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp). This brought us new insights into the composition and nature of comets (Crovisier 1998; Despois 1999; Irvine et al. 2000a; Bockelée-Morvan et al. 2000, 2004).

We present here some of the results of a spectral survey at radio wavelengths made in comet C/1995 O1 (Hale-Bopp). We mainly concentrate on observations made around perihelion, from March to May 1997. In this period, the comet was at 0.91–1.4 AU from the Sun, at 1.3–2.2 AU from the Earth, and had a water outgassing rate from 5 to 11 $\times 10^{30}$ molec. s^{-1}. Three radio telescopes were used: the Caltech Submillimeter Observatory (CSO) on Mauna Kea (Hawaii), the Institut de radioastronomie millimétrique (IRAM) 30-m telescope on Pico Veleta (Spain) and the IRAM interferometer on Plateau de Bure (France; hereafter PdBI), used here in the single-dish mode.

This survey resulted in the detection of most of the cometary molecules already known at radio wavelengths (CO, HCN, CH_3OH, H_2CO, H_2S, CS, CH_3CN, HNC, OCS, HNCO) and of several new cometary molecules (SO, SO_2, HC_3N, NH_2CHO, HCOOH, $HCOOCH_3$) and a new ion (H_3O^+). This was reported by Biver et al. (1999), Lis et al. (1999) and Bockelée-Morvan et al. (1999, 2000). The present paper reports a further analysis of this survey focussed on the study of the non-detected molecules.

Send offprint requests to: J. Crovisier

Table 1. Characteristics of the radio telescopes used for the spectral survey.

telescope	diam. [m]	freq. [GHz]	HPBW [″]	beam efficiency
IRAM 30-m	30	90	27	0.75
		150	16	0.52
		230	11	0.39
IRAM PdBI	5×15	115	42	0.83
		230	21	0.58
CSO	10	230	31	0.72
		345	21	0.65

Table 2. Parameters of comet Hale-Bopp used to derive molecular abundances.

date dd/mm/yy	r_h [AU]	Δ [AU]	$T_{\rm rot}$ [K]	$V_{\rm exp}$ [km s^{-1}]	$Q[H_2O]$ [10^{30} s^{-1}]
1/08/96	3.58	2.73	25	0.60	0.2
15/02/97	1.21	1.73	83	0.93	5.5
1/03/97	1.07	1.49	96	0.98	8.0
15/03/97	0.96	1.34	108	1.02	9.0
1/04/97	0.91	1.35	114	1.05	10.0
15/04/97	0.95	1.51	109	1.03	11.0
1/05/97	1.06	1.77	97	0.98	8.0
15/05/97	1.19	2.01	85	0.94	5.5
1/06/97	1.39	2.27	72	0.88	4.0

$T_{\rm rot}$ and $V_{\rm exp}$ are taken from Biver et al. (1999). $Q[H_2O]$ is from SWAN/SOHO Lyman α data (Combi et al. 2000) and from the observations of the 18-cm line of OH at Nançay (Colom et al. 1999).

During this analysis, two additional cometary molecules have been detected: acetaldehyde, which is discussed in Section 3.5, and ethylene glycol, which is presented in a separate paper (Crovisier et al. 2004). We also report on the detection of the $H_2^{34}S$ isotopic species and on detections of HDO and DCN (which were also detected at the James Clerk Maxwell Telescope, as previously reported by Meier et al. 1998a, 1998b).

Upper limits from previous extensive searches at radio wavelengths were published by Crovisier et al. (1993) for comets C/1989 X1 (Austin) and C/1990 K1 (Levy), and by Lis et al. (1997) for comet C/1996 B2 (Hyakutake). Upper limits for sodium compounds searched for at the CSO in comet Hale-Bopp were also reported by Lis et al. (1999).

Section 2 describes the survey, its strategy of observation and the methods of analysis. The following sections will comment on the results molecule per molecule, for putative parent molecules (Sect. 3), isotopic species (Sect. 4), radicals and ions (Sect. 5). Section 6 is a general discussion of the results.

2. Observations

2.1. The radio telescopes and spectrometers

A description of the telescopes used in the present work is given in Table 1. The receivers and backends are described in more detail in Bockelée-Morvan et al. (2000). Observations were optimized by making the best use of parallel modes and of the versatility of the backends (several receivers with the IRAM 30-m, double sideband mode with the IRAM PdBI and CSO, several backends in parallel with all telescopes). Two kinds of spectra were obtained, most of the time simultaneously: a) high-resolution spectra allowing to resolve the lines, but covering a small spectral range (e.g., 128 channels of 100 kHz); these spectra were aimed at specific lines; b) low-resolution spectra, covering a large spectral range (e.g., 500 channels of 1 MHz); these spectra were devoted to serendipitous searches.

2.2. Strategy of observations

A real spectral survey, i.e. the full coverage of a comprehensive spectral region, was not possible because of the large amount of observing time required to make sensitive observations, and of the limited period when the comet was bright and observable. We thus restricted our observations to selected spectral domains. These domains were chosen so that they encompass as many "interesting" lines as possible.

To help us in choosing the spectral domains to observe, we developed a computer programme (`PAPSYNTHE`) to make synthetic cometary spectra. This programme uses as input the JPL molecular database files (Pickett et al. 1998) and the following parameters: geocentric distance Δ; heliocentric distance r_h; telescope diameter; coma expansion velocity $V_{\rm exp}$; molecular rotational temperature $T_{\rm rot}$; the list of cometary molecules with their hypothetical abundances relative to water and their photodissociation rates; the water production rate $Q[H_2O]$. The molecules are assumed to be at local thermodynamical equilibrium with a constant $T_{\rm rot}$ throughout the coma and to have a parent molecule Haser distribution.

The predictions of `PAPSYNTHE` were used to select the most intense lines of a given species, and to spot combinations of lines of different species that could be observed with the same receiver setting. In many cases, it was possible to include in the spectral domain to be observed a line from an abundant species (such as CH_3OH or H_2CO) which could be easily detected: this provided a direct validation of the observation (check of the telescope pointing and of the receiver tuning).

We estimate that, altogether, a spectral domain of $\approx$ 30 GHz was covered during our observations, which corresponds to about 10% of the region between 85 and 375 GHz. It was found afterwards that strong transitions of several species, which were not considered in our primary choice, were serendipitously observed during our survey. We anticipate that several other species (radicals and

Table 3. Photodissociation rates and dipole moments of the molecules investigated in the present work.

Molecule	photo rate [s^{-1}]	dipole moment [D]			reference
		μ_A	μ_B	μ_C	
$(H_2O)_2$	—	2.633	$\approx 0.$	$\approx 0.$	O
H_2O_2	1.3×10^{-4}	0.657	1.732	—	JPL
CH_3CCH	4.2×10^{-5}	—	0.780	—	JPL
CH_2CO	4.4×10^{-4}	1.422	—	—	JPL
CH_3CHO	7.5×10^{-5}	0.262	2.33	—	O
c–C_2H_4O	—	—	1.88	—	CDMS
C_2H_5OH *trans*	1.8×10^{-5}	0.046	1.438	—	JPL
CH_3OCH_3	3.1×10^{-5}	—	1.302	—	O
CH_3COOH	5.1×10^{-5}	0.86	1.47	—	O
CH_2OHCHO	—	2.55	0.87	—	CDMS
NH_2CH_2COOH I	—	0.91	0.70	—	JPL
HC_5N	—	—	(4.33)	—	JPL
C_2H_5CN	—	3.85	1.23	—	JPL
CH_2NH	—	1.325	1.530	—	JPL
NH_2CN	—	4.327	—	0.961	JPL
NH_2OH	—	0.598	—	0.60	CDMS
HCNO	—	—	3.06	—	O
N_2O	5.9×10^{-6}	—	0.161	—	JPL
NS	—	—	1.81	—	JPL
H_2CS	—	1.649	—	—	JPL
CH_3SH	—	1.312	0.758	—	O
NaCl	—	—	8.97	—	JPL
NaOH	—	—	(6.83)	—	JPL
PH_3	6.1×10^{-5}	—	—	0.574	JPL
HDO	(1.3×10^{-5})	0.657	1.732	—	JPL
DCN	(1.5×10^{-5})	—	2.984	—	JPL
HDCO	(2.0×10^{-4})	2.330	0.195	—	JPL
CH_3OD	(1.3×10^{-5})	0.833	1.488	—	O
CH_2DOH	(1.3×10^{-5})	(0.885)	(1.440)	—	O
NH_2D	(1.3×10^{-4})	0.18	—	1.463	JPL
HDS	(2.5×10^{-4})	0.470	0.974	—	JPL
$H_2^{34}S$	(2.5×10^{-4})	—	(0.974)	—	O
SiC	—	—	(1.7)	—	JPL
SiO	—	—	3.098	—	JPL
HCO	—	1.363	0.700	—	JPL
C_2H	—	—	(0.77)	—	JPL
HNO	—	1.03	1.31	—	JPL
HCP	—	—	0.390	—	JPL
$HOCO^+$	—	(2.0)	(2.8)	—	JPL
H_2COH^+	—	(1.44)	(1.77)	—	CDMS
$HCNH^+$	—	—	(0.29)	—	CDMS
N_2H^+	—	—	3.4	—	JPL

Dipole moment values between parentheses are uncertain (ab initio calculations). Photodestruction rates for isotopologues are assumed equal to those of the main isotopic species. The last column lists which molecular data set was used: "JPL" for the JPL data set, "CDMS" for the Cologne data set and "O" for others (see text).

ions), for which spectral data are still lacking, were also covered in these observations. Further work on our data is still awaiting molecular databases for further species.

2.3. Principle of analysis

As in our previous studies (Crovisier et al. 1993, Lis et al. 1997) we made an extensive use of the `PAPSYNTHE` software and of JPL and Cologne molecular databases (Pickett et al. 1998; Müller et al. 2001). For some species not included in these databases, or for which updated data are available (CH_3OCH_3, CH_3CHO, CH_3OD...), we converted the available molecular data files to the JPL format. For other species without available convenient electronic files (e.g., $(H_2O)_2$), a case-by-case study was necessary (and the analysis is still in progress).

Production rates are evaluated assuming a parent molecule Haser distribution. The expansion velocities ($V_{\rm exp}$) and rotational temperatures ($T_{\rm rot}$) are interpolated from Table 2. The photodissociation rates, when avail-

able, are taken from Crovisier (1994) or Huebner et al. (1992) and are listed in Table 3. They are assumed to be 10^{-4} s^{-1} at 1 AU when unknown. The relative production rates (relative to water – the so-called "abundances") are estimated using water production rates interpolated from Table 2. The line intensities or their upper limits are determined from the observed spectra by integrating over [–2, +2] km s^{-1}, which is expected to cover the full width for unblended lines.

3. Results: various molecules

For each molecule, a selection of the most significant observations are listed line by line in Tables 4–8. The summary of the resulting limits on the relative production rates is listed in Table 9.

3.1. Water dimer ($(H_2O)_2$)

An independent search for microwave lines of the water dimer ($(H_2O)_2$) was made by Scherer et al. (1998) in comet Hale-Bopp. This search was restricted to centimetric lines observable at the Effelsberg radio telescope, which are not the most favourable transitions.

Analyses of the water dimer rotational spectrum were published by Coudert & Hougen (1990) and Zwart et al. (1991). A comprehensive list of transitions was made available to us by Coudert (*pers. comm.*), upon which our search was based. The partition function and line strengths were evaluated as in Scherer et al. (1998). Our upper limit is 0.5% relative to water. This is an order of magnitude lower than the limit (< 6%) obtained by Scherer et al. from the observation of the 2_0E^-–1_0E^+ line at 24.284 GHz.

From theoretical predictions (Crifo & Slanina 1991), water dimers are expected to have small abundances (< 10^{-5} for comet Halley) and our limit is probably not significant.

3.2. Hydrogen peroxide (H_2O_2)

This molecule is not detected in the interstellar medium. Our upper limit is 0.03%.

3.3. Propyne (CH_3CCH)

Propyne (aka methyl acetylene) is the smallest asymmetric hydrocarbon, with a dipole moment of 0.78 D. It can therefore be searched for by its rotational lines. It was sometimes proposed as a parent for the C_3 radical (Krasnopolsky 1991; see also the discussion by Helbert et al. 2000). Its abundance upper limit, however, (0.045%) is slightly smaller than the C_3 production rate (≈ 0.06% from Schleicher et al. 1997).

3.4. Ketene (CH_2CO)

Our abundance upper limit is 0.045% for this molecule.

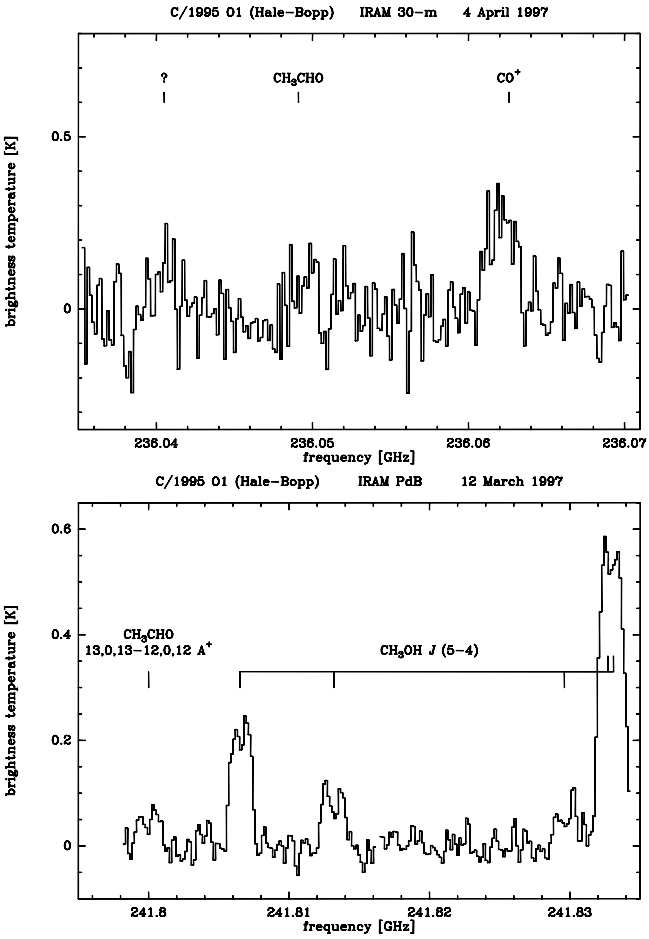

Fig. 1. Observations of acetaldehyde in comet C/1995 O1 Hale-Bopp. **Top:** A marginal line of acetaldehyde observed at IRAM 30-m at 236.0491 GHz, together with a CO^+ line and an unidentified feature. **Bottom:** Rotational lines of methanol and acetaldehyde observed at IRAM PdBI. The x-axis is the frequency in the principal sideband where the methanol lines appear. The acetaldehyde line is at 244.832 GHz in the image sideband.

3.5. Acetaldehyde (CH_3CHO)

Molecular data are taken from Kleiner et al. (1996). At the beginning of the observations, we were not aware of the Kleiner et al. paper and our search for CH_3CHO was based upon the JPL database, in which the frequencies were in error of several MHz for this species.

The detection of CH_3CHO was confirmed during the present work, after the paper of Bockelée-Morvan et al (2000) reporting the radio detection of other molecules was completed. A series of lines were marginally observed with the IRAM 30-m in April and May (one of them is shown in Fig. 1, top). The confirmation came from the serendipitous observation of the $13_{0,13}$–$12_{0,12}$ A^+ line together with methanol lines at PdBI (Fig. 1, bottom). This line is observed at the 7–σ level, on the edge of the band, with a shape closely resembling those of the methanol lines in the same spectrum. The corresponding $13_{0,13}$–$12_{0,12}$ E

line at 244.789 GHz, which was observed the same day, is unfortunately blended with strong methanol lines.

CH_3CHO is next to H_2CO in the aldehyde homologous series. We measure $Q[CH_3CHO] = 0.025\%$ whereas $Q[H_2CO]$ was 1.1% (Bockelée-Morvan et al. 2000). Thus $Q[CH_3CHO]/Q[H_2CO]$ is only $\approx 1/50$. However, this should be mitigated by the fact that most of cometary formaldehyde is coming from a distributed source, the fraction really directly coming from nucleus ices being less than 6% of the total H_2CO (Wink et al. 1999). $[CH_3CHO]/[H_2CO]$ could then be higher than 1/3 in nucleus ices.

From mass spectroscopy investigations of 1P/Halley, Altwegg et al. (1999) reported the "probable" detection of acetaldehyde (or its isomers) with an abundance of 0.5%, much higher than our value for comet Hale-Bopp.

3.6. Ethylene oxide (c–C_2H_4O)

Ethylene oxide (aka oxirane) is an isomer of acetaldehyde. The upper limit we obtain is 0.2%. Thus, $[(c\text{–}C_2H_4O]/[CH_3CHO] < 10$, which is not a stringent limit compared to the ratio $[(c\text{–}C_2H_4O]/[CH_3CHO] = 0.1\text{–}0.4$ observed in interstellar hot cores (Nummelin et al. 1998).

3.7. Ethanol (C_2H_5OH)

The ethanol ground state is the *trans* conformer. Two other conformers, the *gauche* + and *gauche* −, are present at about 57 K above the ground state and are indeed observed in the interstellar medium (Pearson et al. 1998). Our limit (< 0.05%) refers to the *trans* conformer only. At 100 K, the total C_2H_5OH abundance is about 2.1 times that of the ground state conformer. Thus, the limit for total ethanol is 0.1%.

Comparing with the methanol production rate (2.4% as reported by Bockelée-Morvan et al. 2000), we note that $Q[C_2H_5OH]/Q[CH_3OH] < 1/25$.

3.8. Dimethyl ether (CH_3OCH_3)

Molecular data are taken from Groner et al. (1998). The observed lines are blends of AA, EE, AE and EA transitions. The table lists the frequencies for the stronger EE component and the intensities for the sum of the components. Our results are puzzling. There are two hints of detections, each at the 4–σ level, which, if real, would correspond to an abundance of 0.5–0.7%. However, the 17 May observation at IRAM 30-m (together with a strong formaldehyde line) puts a stringent upper limit of 0.1%. We have adopted in Table 9 a conservative upper limit of 0.5%.

3.9. Acetic acid (CH_3COOH)

The search for acetic acid was based upon molecular data from Wlodarczak & Demaison (1988 and *pers. comm.*). A more comprehensive database is now available (Ilyushin et al. 2001, 2003; I. Kleiner, *pers. comm.*) which was used in our analysis.

The upper limit we obtain is 0.06%. This is not much lower than the abundance of formic acid (0.09%; Bockelée-Morvan et al. 2000).

3.10. Glycolaldehyde (CH_2OHCHO)

A line of CH_2OHCHO is marginally present at the 2.7–σ level, which would correspond to an abundance of 0.07%. But the absence of other lines sets up an upper limit of 0.04%.

See also the discussion in Crovisier et al. (2004), where CH_2OHCHO is compared to ethylene glycol ($HOCH_2CH_2OH$), which is detected with an abundance of 0.25%.

Methyl formate ($HCOOCH_3$), acetic acid and glycolaldehyde are isomers. Of these species, only the first one is detected in the comet, with an abundance of 0.08% (Bockelée-Morvan et al. 2000), the others having slightly lower abundance upper limits.

3.11. Glycine (NH_2CH_2COOH)

Glycine (NH_2CH_2COOH) is the simplest amino acid. Considering its interest for astrobiology, this molecule has been actively searched for in the interstellar medium (Miao et al. 1994, Combes et al. 1996, Snyder 1997, Ceccarelli et al. 2000, Hollis et al. 2003 and references therein). Definite detection has been claimed by Kuan et al. (2003). Molecular data for conformers I and II of glycine are available from Lovas et al. (1995) and are listed in the JPL database. The present upper limit has been evaluated for conformer I. Conformer II has a stronger dipole moment, but its equilibrium energy is 700 cm^{-1} higher. From laboratory measurement, Ehrenfreund et al. (2001a) have evaluated the lifetime of glycine (and of other amino acids) to be of the order of a few hours in cometary conditions (at 1 AU), which is similar to our default value of 10 000 s.

Our best upper limits come from three lines expected with similar intensity around 227 GHz. The limit for individual lines is 0.19%. Co-adding the three lines would provide a limit of 0.11%. However, one of the lines has a frequency uncertainty of ≈ 3 MHz. Co-adding the two other lines provides an upper limit of 0.14%, which is the value listed in Table 9.

Table 4. Parameters of molecular lines searched in the present survey.

Transition	frequency	telescope	date	int.	$\int T_b dv$ [mK km s^{-1}]	
	[GHz]		dd/mm/yy	[min]	model	observed
Water dimer $(H_2O)_2$						
12_1E^+–11_1E^-	146.9609	IRAM 30-m	8/04/97	130	21	< 105
$12_{-2}E^-$–$11_{-2}E^+$	147.1302	IRAM 30-m	17/05/97	102	9	< 57
		IRAM 30-m	22/05/97	162	9	< 51
		[CS (3-2) line simultaneously]				
$11_0A_1^-$–$10_0A_1^+$	157.1691	IRAM 30-m	5/04/97	85	27	< 165
		[CH_3OH lines simultaneously]				
Hydrogen peroxide H_2O_2						
$4_{1,3}$–$3_{0,3}$	143.7126	IRAM 30-m	21/05/97	157*	252	< 78
$6_{1,5}$–$5_{0,5}$	251.9147	CSO	3/04/97	18*	190	< 90
Propyne CH_3CCH						
13_0–12_0	222.1670	IRAM PdB	18/03/97	34	71	< 23
[and other lines of the 13–12 series]						
14_0–13_0	239.2522	CSO	27/03/97	32	37	< 250
[and other lines of the 14–13 series]		[simultaneous lines of CH_3CN]				
Ketene CH_2CO						
$11_{1,11}$–$10_{1,10}$	220.1782	IRAM 30-m	15/05/97	50*	294	< 323
		IRAM 30-m	22/05/97	135*		< 93
$13_{1,13}$–$12_{1,12}$	260.1948	CSO	16/04/97	10	51	< 192
		CSO	17/04/97	44		< 220
Acetaldehyde CH_3CHO						
$11_{1,10}$–$10_{1,9}A^-$	216.6302	IRAM 30-m	16/05/97	45*	859	264 ± 67
		IRAM 30-m	22/05/97	102*		66 ± 24
$12_{2,11}$–$11_{2,10}A^-$	230.3019	IRAM 30-m	22/05/97	27*	876	126 ± 42
$12_{0,12}$–$11_{0,11}A^+$	226.5927	IRAM 30-m	11/04/97	65*	944	175 ± 66
$12_{1,11}$–$11_{1,10}A^-$	236.0491	IRAM 30-m	4/04/97	128*	1064	219 ± 59
		CSO	22/02/97	22	268	< 47
$13_{2,1}2$–$12_{2,11}A^-$	249.3239	CSO	22/04/97	38	204	< 50
$13_{3,10}$–$12_{3,9}A^-$	251.4892	CSO	21/04/97	32	182	< 55
$13_{0,13}$–$12_{0,1}2A^+$	244.8322	IRAM PdBI	12/03/97	16*	508	122 ± 17
		[line near the band edge]				
$13_{0,13}$–$12_{0,12}E$	244.7892	IRAM PdBI	12/03/97	16*	508	—
		[line blended with methanol lines]				
Ethylene oxide c–C_2H_4O						
$8_{1,7}$–$7_{2,6}$	254.2317	CSO	21/04/97	16	11	< 95
$8_{2,7}$–$7_{1,6}$	254.2357				6	< 95
$9_{0,9}$–$8_{1,8}$	263.2925	CSO	8/04/97	22	9	< 50
$9_{1,9}$–$8_{0,8}$	263.2925				15	
Ethanol C_2H_5OH *trans*						
$14_{1,14}$–$13_{0,13}$	235.9833	IRAM 30-m	4/04/97	113*	290	< 170
$4_{4,1}$–$3_{3,0}$	252.9514	CSO	23/04/97	40*	43	< 75
$4_{4,0}$–$3_{3,1}$	252.9524				43	
		[Simultaneous CH_3OH lines]				

Each entry gives:
- the transition denomination;
- the frequency (in GHz);
- the telescope;
- the date of the observation;
- the integration time ("*" denotes observations made at high spectral resolution);
- the expected line intensity (in mK km s^{-1}) from the PAPSYNTHE model for a production rate of 10^{28} s^{-1};
- the 3–σ upper limit (in mK km s^{-1}) or the line area with its 1–σ error in case of (marginal) detection.

This upper limit ($\approx$ 0.15% in number relative to water) corresponds to $\approx$ 0.3% in mass in cometary ice, or 0.05% in mass in cometary material if we assume a dust-to-ice ratio of 5 (estimates of the dust-to-gas ratio in this comet range from 2 to 10; Grün et al. 2001, Weiler et al. 2003). In CI and CM type carbonaceous chondrites, which could be akin to cometary material, glycine is among the most abundant amino acids, the other ones being alanine, γ-amino-n-butyric acid and aminoisobutyric acid. The glycine concentration is $\approx 7 \times 10^{-7}$ in mass in the CI-type meteorites Orgueil and Ivuna (Ehrenfreund et al. 2001b), $\approx 2.5 \times 10^{-6}$ in the CM-type meteorites Murchison and Murray (Cronin & Chang 1993). In this respect, our limit in comet Hale-Bopp is hardly significant. On the other hand, the abundance of glycine measured by Kuan et al. (2003) in the Galactic Centre (Sag B2) and in Orion KL is comparable to other minor gas phase species such as formic acid. We note that our limit on glycine, which is at the level of $\approx$ 1.5 the abundance of HCOOH, is quite relevant in this context.

3.12. Cyanodiacetylene (HC_5N)

Our upper limit for HC_5N is 0.003%, whereas the abundances of HCN and HC_3N are 0.25 and 0.020, respectively (Bockelée-Morvan et al. 2000). Thus, $[HC_5N]/[HC_3N] < 0.14$ whereas $[HC_3N]/[HCN] = 0.08$, showing the continuous decrease of the abundance of cyanopolyynes with increasing carbon chain. See Section 6 and Fig. 6.

3.13. Methanimine (CH_2NH)

Our upper limit for CH_2NH is 0.03%.

This molecule was proposed as a possible parent for HNC (the unstable isomer of HCN) by Irvine et al. (1998), but their search for CH_2NH was inconclusive. The origin of cometary HNC is a mystery. Its abundance relative to HCN varies from comet to comet and increases with decreasing heliocentric distance (Biver et al. 1999, 2002; Irvine et al. 1999). Chemical models fail to explain its production from the conversion of HCN in the coma (Rodgers & Charnley 2001).

Our upper limit corresponds to $Q[CH_2NH] < 3. \times 10^{27}$ s^{-1} near perihelion. At that time, Q[HNC] was about 3–4 $\times 10^{27}$ s^{-1} (Biver et al. 1999), *assuming a parent molecule distribution*; if this species is indeed coming from an extended source, its production rate is underestimated. Thus, even if the yield for the $CH_2NH \rightarrow HNC + 2\ H$ photodissociation channel is unity, our observation seems to exclude the production of all the cometary HNC from methanimine[1].

A related *CHN* molecule is methylamine (CH_3NH_2). A comprehensive data set of microwave lines is still lacking for this species. The published lines of this molecule were not covered in our survey.

[1] Unless the lifetime of CH_2NH is significantly smaller than our assumed value of 10^4 s, in which case we would have underestimated its production rate.

3.14. Ethyl cyanide (C_2H_5CN)

Our upper limit (0.01%) is half the abundances of the detected carbon-chain cyanides CH_3CN and HC_3N (0.02% from Bockelée-Morvan et al. 2000).

3.15. Cyanamide (NH_2CN)

Our upper limit is 0.004%. This very low value is due to the high dipole moment of the molecule.

3.16. Hydroxylamine (NH_2OH)

Although not detected in the interstellar medium, hydroxylamine is suspected to be an important constituent of interstellar ices (Charnley et al. 2001). Our upper limit is 0.25%, somewhat below the abundance of ammonia (0.7% from Bird et al. 1999).

3.17. Fulminic acid (HCNO)

Fulminic acid is an isomer of isocyanic acid (HNCO, observed with an abundance of 0.1%; Bockelée-Morvan et al. 2000). Molecular data are from Winnewisser & Winnewisser (1971). This species has not been detected in the interstellar medium.

Our upper limit corresponds to an isomeric ratio Q[HCNO]/Q[HNCO] $< 1/60$. The good limit is due to the high dipole moment (3.06 D) of this linear molecule.

3.18. Nitrous oxide N_2O

Nitrogen oxides have small dipole moments and their radio lines cannot be easily observed. Our limit for N_2O (0.23%) is thus not stringent. Unfortunately, nitric oxide NO was not covered in the present survey.

3.19. NS radical

The NS radical was detected by Irvine et al. (2000b) in comet Hale-Bopp on 22 March at the James Clerk Maxwell Telescope (JCMT) (J(15/2–13/2) e and f transitions at 346 GHz). No plausible parent could be found which would produce this radical by photodissociation. Chemical models do not predict any significant production of NS in the coma (Canaves et al. 2002). The presence of this radical is thus a puzzle. A direct production from cometary ices has been invoked (Irvine et al. 2000b).

We could not confirm this detection (serendipitous observation of the J(11/2–9/2) transition at 254 GHz with the CSO on 21 April). Our upper limit (0.01%) is about twice lower than the abundance derived by Irvine et al. (assuming in both cases a parent molecule distribution). One should consider, however, the unknown spatial dis-

ht

Table 5. Parameters of molecular lines searched in the present survey (continued).

Transition	frequency	telescope	date	int.	$\int T_b dv$ [mK km s^{-1}]	
	[GHz]		dd/mm/yy	[min]	model	observed
Dimethyl ether CH_3OCH_3						
$7_{1,7}$–$6_{0,6}$	147.0249	IRAM 30-m	8/04/97	130*	41	216 ± 54
$10_{4,6}$–$10_{3,7}$	203.5703	IRAM 30-m	3/04/97	150*	59	< 153
$4_{3,2}$–$3_{2,2}$	222.4226	CSO	23/04/97	24*	10	< 100
$4_{3,1}$–$3_{2,2}$	222.4337	CSO	24/04/97	6	10	< 180
$12_{1,12}$–$11_{0,11}$	225.5991	CSO	23/04/97	24*	34	243 ± 69
		IRAM PdB	16/03/97	28		< 80
		IRAM 30-m	17/05/97	244	97	< 100
		[Simultaneous H_2CO line at 225.697 GHz]				
Acetic acid CH_3COOH						
$18_{*,16}$–$17_{*,15}A$	216.8116	IRAM 30-m	21/05/97	102*	120	< 150
$19_{*,17}$–$18_{*,16}A$	227.4542	IRAM 30-m	5/04/97	165*	150	< 89
Glycolaldehyde CH_2OHCHO						
$14_{0,14}$–$13_{1,13}$	143.6409	IRAM 30-m	21/05/97	120	57	< 75
$14_{1,14}$–$13_{0,13}$	143.7656				57	< 75
$13_{2,12}$–$12_{1,11}$	146.0193	IRAM 30-m	17/05/97	105	40	< 55
$20_{0,20}$–$19_{1,19}$	203.2668	IRAM 30-m	03/04/97	152	229	320 ± 120
$20_{1,20}$–$19_{0,19}$	203.2701				229	
$20_{3,17}$–$19_{4,16}$	218.2605	IRAM 30-m	21/05/97	55	44	< 150
$7_{6,2}$–$6_{5,1}$	220.1966	IRAM 30-m	22/05/97	135	87	< 75
$7_{6,1}$–$6_{5,2}$	220.1969				87	
Glycine I NH_2CH_2COOH						
$35_{*,31}$–$34_{*,32}$	222.611	CSO	23/04/97	24	16	< 135
		CSO	24/04/97	6		< 180
$12_{11,*}$–$11_{10,*}$	227.3609	IRAM 30-m	5/04/97	310	35	< 66
$33_{7,*}$–$32_{7,*}$	227.3628				35	< 66
$33_{14,*}$–$32_{14,*}$	227.5478				38	< 66
[and many others]						
Cyanodiacetylene HC_5N						
34–33	90.5262	IRAM PdB	13/03/97	24	360	< 30
		IRAM 30-m	5/04/97	295*	1125	< 35
40–39	106.4994	IRAM 30-m	4/04/97	150*	1600	< 53
54–53	143.7663	IRAM 30-m	21/05/97	157*	1295	< 64
59–58	157.0743	IRAM 30-m	5/04/97	85	2240	< 180
Ethyl cyanide C_2H_5CN						
$25_{3,22}$–$24_{3,21}$	227.7808	IRAM 30-m	5/04/97	310	704	< 66
Methanimine CH_2NH						
$1_{1,1}$–$0_{0,0}$	225.5548	IRAM 30-m	17/05/97	244	290	< 65
$6_{1,5}$–$6_{0,6}$	226.5484	IRAM 30-m	11/04/97	65*	545	< 190
$6_{1,6}$–$5_{1,5}$	251.4212	CSO	21/04/97	32	115	< 55
$4_{1,3}$–$3_{1,2}$	266.2701	CSO	8/04/97	44*	220	< 75

See description in the footnotes of Table 4.

tribution of this radical, the fact that different lines were observed, and possible non-thermal excitation.

3.20. Thioformaldehyde (H_2CS)

Thioformaldehyde (H_2CS) was detected in comet Hale-Bopp by Woodney et al. (1999) with the National Radio Astronomical Observatory (NRAO) 12-m telescope at Kitt Peak. This detection relies on the observation of a single line with a limited S/N.

We could not confirm this detection. Our upper limit is 0.04% and is similar to the abundance (0.038%) we derive from the Woodney et al. observation, using the same model parameters. Woodney (*pers. comm.* quoted by Bockelée-Morvan et al. 2000) derived an abundance of 0.02%, but an abundance of 0.05% is reported in Woodney (2000). The photodissociation rate of H_2CS is unknown.

Table 6. Parameters of molecular lines searched in the present survey (continued).

Transition	frequency	telescope	date	int.	$\int T_b dv$ [mK km s^{-1}]	
	[GHz]		dd/mm/yy	[min]	model	observed
Cyanamide NH_2CN						
$11_{1,11}$–$10_{1,10}$	218.4618	IRAM 30-m	3/04/97	53*	4760	< 200
Hydroxylamine NH_2OH						
$5_{1,5}$–$4_{1,4}$	251.6774	CSO	5/04/97	68	28	< 70
$5_{0,5}$–$4_{0,4}$	251.8385				31	< 70
Fulminic acid HCNO						
11–10	252.2965	CSO	22/04/97	38*	3800	< 60
Nitrous oxide N_2O						
10–9	251.2116	CSO	21/04/97	32*	29	< 67
11–10	276.3278	CSO	7/04/97	32	35	< 92
Radical NS						
5/2–3/2 *c*	115.153	IRAM 30-m	12/05/97	15	174	< 420
		[simultaneous CO(1–0) line]				
11/2–9/2	253.968	CSO	21/04/97	32	785	< 82
		[simultaneous CH_3OH lines]				
15/2–13/2 *e*	345.823	JCMT	22/03/97		4380	= 640 ± 110
15/2–13/2 *f*	346.220	JCMT	22/03/97		4380	= 480 ± 60
		[For comparison: detection by Irvine et al. 2000b]				
Thioformaldehyde H_2CS						
$8_{1,8}$–$7_{1,7}$	270.5207	CSO	19/03/97	16*	440	< 200
			27/03/97	22		< 150
		[simultaneous HCO^+ line – very close]				
$9_{1,9}$–$8_{1,8}$	304.3060	CSO	4/04/97	40	600	< 240
		[simultaneous CH_3OH lines]				
$7_{1,6}$–$6_{1,5}$	244.0478	NRAO 12-m	23/03/97		435	= 167 ± 39
		[For comparison: detection by Woodney et al. 1999]				
Methyl mercaptan CH_3SH						
9_0–8_0 A^+	227.3264	IRAM 30-m	5/04/97	310	190	< 24
9_2–8_2 A^-	227.5314	IRAM 30-m	5/04/97	310*	155	< 72
other lines		IRAM PdB	6/03/97	8		< 80
of the 9–8 series		IRAM PdB	11/03/97	27		< 60
		[simultaneous HC_3N line at 227.4189 GHz]				
10_4–9_4 A^-	252.8415	CSO	23/04/97	40		< 45
		[simultaneous CH_3OH lines]				
Phosphine PH_3						
1_0–0_0	266.9447	CSO	2/08/96	96*	13	< 21

See description in the footnotes of Table 4.

Woodney used $2.\times10^{-4}$ s^{-1}, i.e. the same as that of H_2CO, whereas we used our default value of 10^{-4} s^{-1}.

3.21. Methyl mercaptan (CH_3SH)

Molecular data are taken from Bettens et al. (1999). The upper limit is 0.05%, which corresponds to $Q[CH_3SH]/Q[CH_3OH] < 0.02$, not significantly smaller than the cosmic abundance ratio $[S]/[O] = 0.032 \pm 0.10$ (Grevesse & Sauval 1998).

3.22. Phosphine (PH_3)

Phosphine is detected in the atmospheres of Jupiter and Saturn, but not in interstellar clouds. No phosphorous species has ever been observed in comets.

Phosphine was searched for through its fundamental rotational line 1_0–0_0 at 266.945 GHz at the CSO. The observation took place on 2 August 1996 when the comet was still at 3.6 AU from the Sun and was not repeated, unfortunately. The upper limit is $Q[PH_3] < 3.2 \times 10^{26}$ s^{-1}. This corresponds to $Q[PH_3]/Q[H_2O] < 0.0016$, which is not significant compared to the cosmic elemental abundance ratio $[P]/[O] = 4.2 \pm 0.8 \times 10^{-4}$ (Grevesse & Sauval 1998).

However, PH_3 is a very volatile species. It sublimates at an equilibrium temperature of 41 K under cometary

Table 7. Parameters of molecular lines searched in the present: survey: deuterated and isotopic species.

Transition	frequency	telescope	date	int.	$\int T_b dv$ [mK km s^{-1}]	
	[GHz]		dd/mm/yy	[min]	model	observed
Deuterated water HDO						
$3_{1,2}$–$2_{2,1}$	225.8967	IRAM PdB	9,16/03/97	40	—	105 ± 21
		IRAM 30-m	17/05/97	244*	—	90 ± 20
$2_{1,1}$–$2_{1,2}$	241.5616	CSO	27/03/97	85*	—	< 55
Deuterated hydrogen cyanide DCN						
2–1	144.8280	IRAM 30-m	29/05/97	145*	—	< 105
3–2	217.2385	IRAM 30-m	9,10/04/97	253*	—	217 ± 57
		[simultaneous CH_3OH line]				
5–4	362.0465	CSO	6/04/97	43*	—	< 335
			24/04/97	13*	—	< 680
Deuterated formaldehyde HDCO						
$1_{1,1}$–$0_{0,0}$	227.6681	IRAM 30-m	5/04/97	310	4	< 90
$7_{1,6}$–$7_{0,7}$	252.7264	CSO	23/04/97	40	2	< 70
$6_{0,6}$–$5_{1,5}$	252.9639				2	< 70
		[Simultaneous CH_3OH lines]				
$4_{2,2}$–$3_{2,1}$	259.0349	CSO	21/04/97	10	298	< 150
		[Simultaneous CH_3OH and SO lines]				
Deuterated methanol CH_3OD						
5_1 A^-–5_0 A^+	143.7417	IRAM 30-m	21/05/97	120*	178	< 62
5_0 A^+–4_0 A^+	226.5387	IRAM 30-m	11/04/97	65	160	< 210
5–4 E series	226.277				266	280 ± 71
5_{-2} E–5_{-1} E	270.5814	CSO	27/03/97	22	86	< 270
6_2 A^+–6_1 A^-	307.3682	CSO	4/04/97	40	122	< 250
Deuterated methanol CH_2DOH						
$5_{1,5}$–$4_{1,4}$ e_0	220.0719	IRAM 30-m	22/05/97	135	82	< 75
$5_{1,4}$–$4_{1,3}$ e_1	225.6676	IRAM 30-m	17/05/97	244	62	< 60
$5_{1,4}$–$4_{1,3}$ e_0	226.8184	IRAM 30-m	11/04/97	65	153	< 89
Deuterated ammonia NH_2D						
$3_{2,2}$–$3_{1,2}$	216.5626	IRAM 30-m	16/05/97	45	180	< 90
			29/05/97	155	186	< 60
Deuterated hydrogen sulphide HDS						
$1_{0,1}$–$0_{0,0}$	244.5556	CSO	27/03/97	86	12	< 35
Hydrogen sulfide H_2S, ^{34}S *variety*						
$1_{1,0}$-$1_{0,1}$	167.9105	IRAM 30-m	9–10/11/96	160*	—	107 ± 24

See description in the footnotes of Table 4.

conditions, comparable to that of the hypervolatiles CO (24 K), CH_4 (31 K) or C_2H_6 (44 K). At $r_h = 3.6$ AU, the sublimation of water is inhibited by the low equilibrium temperature of the cometary nucleus, whereas that of the hypervolatiles is not. If we rescale the $[PH_3]/[H_2O]$ ratio according to the $[CO]/[H_2O]$ evolution with heliocentric distance (as measured by Biver et al. 1999), we would obtain $Q[PH_3]/Q[H_2O] < 1.6 \times 10^{-4}$ at $r_h \approx 1$ AU, now smaller than the cosmic [P]/[H] ratio.

3.23. Sodium species (NaCl and NaOH)

Atomic sodium in comets is conspicuous in the coma (or, for comet Hale-Bopp as a "third type" tail) through its D_1 and D_2 lines observed in comets at $r_h < 1.5$ AU. Its origin, however, is still a mystery. Direct desorption from dust grains or degradation of parent molecules have been invoked. Since the [Na]/[O] cosmic ratio is 1/300 (Grevesse & Sauval 1998) and the Na production rate observed in the comet was only 5×10^{-6} relative to water (Cremonese et al. 1997), most of the cometary sodium must remain trapped in refractories.

The upper limits listed in Table 9 for NaOH and NaCl are those reported in Lis et al. (1999) and the detail of the observations is not repeated here. The limits are very low because of the very large dipole moments of these linear molecules (6.8 and 9.0 D, respectively). They are comparable to the Na production rate observed in the comet, so that no definite conclusion can be drawn from our observations on the nature of the Na source in comets. Furthermore, these limits were evaluated assuming lifetimes of 10^4 s for these molecules. The real lifetimes are likely to be much shorter (Cremonese et al. 2002), in which case our upper limits are underestimated.

Table 8. Parameters of molecular lines searched in the present: survey: radicals and ions.

Transition	frequency	telescope	date	int.	$\int T_b dv$ [mK km s^{-1}]	
	[GHz]		dd/mm/yy	[min]	model	observed
Radical SiC						
$^3\Pi_2$ J(6–5) e,f	236.2876	CSO	27/03/97	32	615	< 250
Radical SiO						
5–4	217.1050	IRAM 30-m	9,10/04/97	253	18000	< 250
7–6	303.9270	CSO	4/04/97	40	9000	< 250
Radical HCO						
$3_{0,3}$–$2_{0,2}$	260.0603	CSO	16/04/97	10	120	< 190
		CSO	17/04/97	44		< 220
Ethynyl radical C_2H						
N(3–2) J(7/2–5/2) F(4–3)	262.0042	CSO	21/04/97	10	see text	
N(3–2) J(7/2–5/2) F(2–2)	262.0065					
N(3–2) J(5/2–3/2) F(3–2)	262.0650					
N(3–2) J(5/2–3/2) F(2–1)	262.0675					
Nitroxyl HNO						
$3_{0,3}$–$2_{0,2}$	244.3641	CSO	27/03/97	85*		< 52
Methylidynephosphine HCP						
7–6	279.6347	CSO	7/04/97	32	115	< 100
Protonated carbon dioxide $HOCO^+$						
$5_{0,5}$–$4_{0,4}$	106.9136	IRAM PdB	20/03/97	34*	85	< 21
		IRAM PdB	21/03/97	58*		< 19
Protonated formaldehyde H_2COH^+						
$1_{1,0}$–$1_{0,1}$	168.4011	IRAM 30-m	3/04/97	224*		< 180
Protonated hydrogen cyanide $HCNH^+$						
3–2	222.3293	IRAM 30-m	26/05/97	53*	86	< 500
Protonated dinitrogen N_2H^+						
3–2	279.5117	CSO	7/04/97	32	9400	< 100

See description in the footnotes of Table 4.

4. Results: isotopic species

The enrichment of deuterium in cometary and interstellar molecules is characteristic of the fractionation which occurred during the formation of these molecules[2]. Up to now, HDO and DCN are the only deuterated molecules detected in comets (Bockelée-Morvan et al. 1998, Meier et al. 1998a, 1998b). For comprehensive discussions of this topic, see Meier & Owen, 1999 and Altwegg & Bockelée-Morvan (2003). [D]/[H] in cometary water was found to be 3×10^{-4} in three comets (1P/Halley, C/1996 B2 (Hyakutake), C/1995 O1 (Hale-Bopp)), enriched by a factor of ≈ 10 over the protosolar value. [D]/[H] in HCN was still higher (2×10^{-3}) in comet Hale-Bopp. The deuterium enrichment could be even higher in other molecules, as is observed in interstellar clouds (Table 10).

4.1. Deuterated water (HDO)

HDO was detected in comet Hale-Bopp at the JCMT through its 1_{10}–0_{00} submillimetric line at 465 GHz, as was reported by Meier et al. (1998a). The observation of this line from the ground requires exceptionally good weather conditions.

Millimetric lines of HDO between low-energy levels are the 1_{10}–1_{11} line at 80.578 GHz (which was then unfortunately not accessible to the IRAM receivers), the 3_{12}–2_{21} line at 225.897 GHz, and the 2_{11}–2_{12} line at 241.562 GHz. These lines are much weaker (by a factor of 10 or more) than the submillimetric lines of HDO. The 242 GHz line was observed together with 5_K–4_K methanol lines at the CSO on 27 March, but was not detected. The 226 GHz line was serendipitously detected at the edge of a low-resolution backend of the PdB interferometer on 9 and 16 March (Fig. 2, top). Despite the low velocity resolution and the signal-to-noise ratio of the line of ≈ 5 only, confidence in the detection comes from the presence of the line in the two independent observations. This line is also present at the 4.5–σ level in a high-resolution spectrum obtained on 17 May at the IRAM 30-m (Fig. 2, bottom).

The HDO production rates were computed using an excitation model which includes solar IR pumping of the vibrational bands and collisional excitation by electrons and neutrals (see Bockelée-Morvan et al. 1998; Meier et al. 1998a). Inferred Q[HDO] values are $9.4 \pm 1.9 \times 10^{27}$,

[2] Note that the [D]/[H] ratio in a molecule H_nR is $\frac{1}{n}\frac{[H_{n-1}DR]}{[H_nR]}$, not $\frac{[H_{n-1}DR]}{[H_nR]}$. Thus, $[D]/[H]_{H_2O} = 0.5$ $[HDO]/[H_2O]$

Table 9. Summary of molecular upper limits in comet Hale-Bopp derived from the present work.

molecule	$[X]/[H_2O]$
H_2O	100
$(H_2O)_2$	< 0.5
H_2O_2	< 0.03
CH_3CCH	< 0.045
CH_2CO	< 0.032
CH_3CHO	$= 0.025$
c–C_2H_4O	< 0.20
C_2H_5OH	< 0.10
CH_3OCH_3	< 0.45
CH_3COOH	< 0.06
CH_2OHCHO	< 0.04
NH_2CH_2COOH I	< 0.15
HC_5N	< 0.003
C_2H_5CN	< 0.010
CH_2NH	< 0.032
NH_2CN	< 0.004
NH_2OH	< 0.25
HCNO	< 0.0016
N_2O	< 0.23
NS	< 0.01
H_2CS	< 0.04
CH_3SH	< 0.05
NaOH	< 0.0003
NaCl	< 0.0008
PH_3	< 0.16
HDCO	< 0.05
CH_3OD	< 0.07
CH_2DOH	< 0.06
NH_2D	< 0.08
HDS	< 0.3

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

$< 3.5 \times 10^{27}$, and $4.7 \pm 1.1 \times 10^{27}\,s^{-1}$ for 9 and 16 March, 27 March, and 17 May, respectively. This translates into $[D]/[H]_{H_2O} = 5.2 \pm 1.2 \times 10^{-4}$, $< 1.8 \times 10^{-4}$, and $= 4.1 \pm 1.0 \times 10^{-4}$, respectively. The uncertainties given in these numbers include a 10% uncertainty in $Q([H_2O])$ values. For comparison, Meier et al. (1998a) deduced $[D]/[H]_{H_2O} = 3.3 \pm 0.8 \times 10^{-4}$ from the 465 GHz line observed on 5 April, using the same modelling for HDO excitation. Therefore, the measurements obtained from the 226 GHz and 465 GHz lines agree within the error bars.

On the other hand, the low upper limit of 1.8×10^{-4} we derive from the 242 GHz line is puzzling. The simultaneous observation of CH_3OH lines provides a methanol production rate consistent with contemporary independent measurements, thereby excluding a decrease of cometary activity at the very moment of the HDO observations. Model calculations show that the derived Q[HDO] is not very sensitive to assumed model parameters. So, we do not have any evident explanation for this conflicting result.

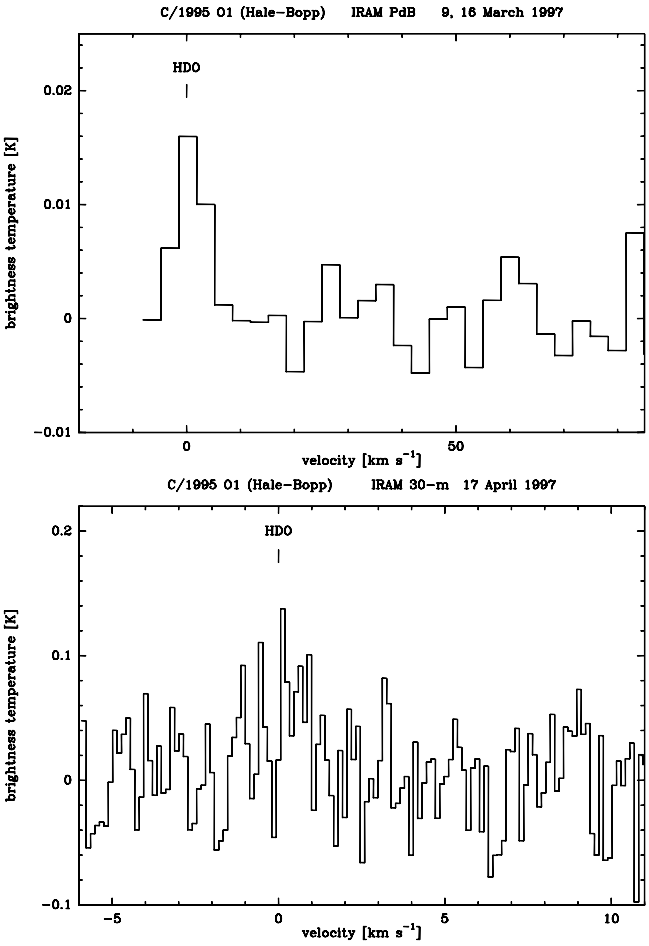

Fig. 2. The 3_{12}–2_{21} line of HDO at 225.897 GHz observed at the PdBI in comet Hale-Bopp (top) and at the IRAM 30-m telescope (bottom).

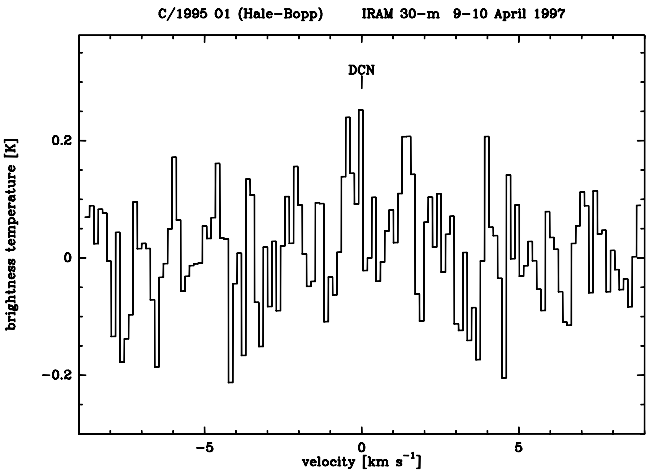

Fig. 3. The J(3–2) line of DCN at 217.238 GHz observed at the IRAM 30-m telescope in comet Hale-Bopp.

4.2. Deuterated hydrogen cyanide (DCN)

We searched for DCN through its J(2–1) and (3–2) transitions at IRAM 30-m, and its J(5–4) transition at the CSO. A tentative detection at the 4–σ level was obtained near

Table 10. [D]/[H] ratios in deuterated molecules in interstellar clouds and in comets.

Molecule	TMC–1 (10 K)	OMC–1 (∼ 60 K)	hot cores (∼ 200 K)	comets
HDO			> 0.002	0.0003
DCN	0.023	0.02	0.005	0.002
NH_2D	< 0.02		0.003	< 0.04
HDCO	0.015	0.02	0.14	< 0.05
CH_3OD			0.03	< 0.03
CH_2DOH			0.04	< 0.008
HDS			< 0.001	< 0.2

Values for TMC–1, OMC–1 and hot cores are from Millar (2000) (from Hatchell et al. 1999 for HDS). Values for comets are from Bockelée-Morvan et al. (1998) and Meier et al. (1998a) for HDO, from Meier et al. (1998b) for DCN, and from the present work for upper limits.

perihelion for the $J(3–2)$ line. It is reported in Table 7 and shown in Fig 3. It corresponds to $Q[\mathrm{DCN}] = 7.9 \pm 2.1 \times 10^{25}$ s^{-1} and, compared to the simultaneous measurement of $Q[\mathrm{HCN}]$, to $[\mathrm{D}]/[\mathrm{H}]_{\mathrm{HCN}} = 2.3 \pm 0.6 \times 10^{-3}$. For consistency, we have used the same modelling (described by Biver et al. 1999) for HCN and DCN, instead of **PAPSYNTHE**. This value is in excellent agreement with the measurement of Meier et al. (1998b) ($2.3 \pm 0.6 \times 10^{-3}$). The upper limits for undetected lines are also higher than this value ([D]/[H] $< 7.7 \times 10^{-3}$ and $< 3.6 \times 10^{-3}$ for the $J(2–1)$ and $J(5–4)$ lines, respectively).

4.3. Deuterated formaldehyde (HDCO)

HDCO has two dipole moment components, μ_A = 2.32 D and μ_B = 0.18 D, corresponding to a-type and b-type transitions. Hence, a-type transitions are two orders of magnitude stronger than b-type transitions. Unfortunately, most of the transitions which were searched for were b-type. An a-type transition ($4_{22}–3_{21}$) was, however, observed serendipitously at the CSO, but the integration time was short and the limit is not very good. Our upper limit on HDCO comes from this observation. H_2CO (and so should be HDCO) is observed to come, in part, from a distributed source of unknown nature (Colom et al. 1992; Bockelée-Morvan et al. 2000). This hampers the determination of the production rates of H_2CO and HDCO. Our determination $[\mathrm{HDCO}]/[\mathrm{H_2CO}] < 0.1$, corresponding to $[\mathrm{D}]/[\mathrm{H}] < 0.05$, however, is based upon the comparison of the column densities and does not suffer from this difficulty.

4.4. Deuterated methanol (CH_3OD, CH_2DOH)

The molecular data for CH_3OD are taken from Anderson et al. (1988). A computer file of the CH_3OD transitions, provided by E. Herbst, (*pers. comm.*) was converted to the JPL catalogue format. Our upper limit is based upon the $5_1–5_0A$ line at 143.741 GHz observed at the IRAM 30-m.

For CH_2DOH we also used a list of transitions provided by E. Herbst, (*pers. comm.*), described in Parise et al. (2002). Note that if the deuterium atom can replace with the same probability the four hydrogen atoms of CH_3OH (as expected from models involving grain chemistry; Charnley et al. 1997), one would expect $[\mathrm{CH_2DOH}]$ = 3 $[\mathrm{CH_3OD}]$. The observation of CH_2DOH is thus more sensitive for the measurement of the [D]/[H] ratio. Jacq et al. (1993) observed $[\mathrm{CH_2DOH}]/[\mathrm{CH_3OD}]$ = 1.1–1.5 in Orion–IRc2, whereas Parise et al. (2002) observed $[\mathrm{CH_2DOH}]/[\mathrm{CH_3OD}] = 20 \pm 14$ in the protostar IRAS 162931–2422. We obtain $[\mathrm{D}]/[\mathrm{H}]_{\mathrm{CH_3OH}} < 0.03$ from CH_3OD, < 0.008 from CH_2DOH. For comparison, Eberhardt et al. (1994) measured $[\mathrm{D}]/[\mathrm{H}]_{\mathrm{CH_3OH}} < 0.01$ from mass spectroscopy in comet Halley (mass spectroscopy cannot distinguish CH_2DOH from CH_3OD).

4.5. Other deuterated species (NH_2D, HDS)

NH_2D has not been searched for on purpose. A line serendipitously observed at IRAM 30-m does not provide a very stringent limit ($[\mathrm{D}]/[\mathrm{H}]_{\mathrm{NH_3}} < 0.04$; however, $[\mathrm{D}]/[\mathrm{H}]_{\mathrm{NH_3}}$ as high as 0.05 has been recently observed in NH_3 in dark clouds by Saito et al. 2000).

For HDS, only the fundamental transition $1_{01}–0_{00}$ at 244.556 GHz was searched for, at the CSO. The upper limit is not very significant ($[\mathrm{D}]/[\mathrm{H}]_{\mathrm{H_2S}} < 0.2$).

Although no detection could be achieved, the upper limits obtained on HDCO, CH_3OD and CH_2DOH, which are the most significant, show that these molecules are less deuterium enriched in comets than in interstellar clouds, confirming the result obtained for HDO and DCN (Table 10). This possibility results from reprocessing in the Solar Nebula, as proposed by Hersant et al. (2001): gas-phase H_2O and HCN, originating from ices infalling from the presolar cloud, underwent isotopic exchanges with H_2 in the inner Solar Nebula; reprocessed gas then diffused by turbulence to the outer regions where comets formed. The rate of isotopic exchange is species dependent and less efficient for HCN.

4.6. Other isotopic species ($H_2{}^{34}S$)

Jewitt et al. (1997) measured $[^{12}\mathrm{C}]/[^{13}\mathrm{C}]$, $[^{14}\mathrm{N}]/[^{15}\mathrm{N}]$ and $[^{32}\mathrm{S}]/[^{34}\mathrm{S}]$ ratios from the observations of radio lines of $H^{13}CN$, $HC^{15}N$ and $C^{34}S$ with the JCMT. Our observation of $H^{13}CN$ at the CSO is discussed by Lis et al. (1999).

$H_2^{34}S$ was searched for and tentatively detected at the 4–σ level on 9 and 10 Nov. 1996 at IRAM through its $1_{10}–1_{01}$ line at 167.910 GHz (Fig. 4). The molecular data are taken from Helminger et al. (1973). A direct comparison with the corresponding line of $H_2^{32}S$ (which is optically thin) observed at the same moment gives $[^{32}\mathrm{S}]/[^{34}\mathrm{S}] = 16.5 \pm 3.5$. This is lower than the value $[^{32}\mathrm{S}]/[^{34}\mathrm{S}] = 27 \pm 3$ observed by Jewitt et al. (1997) for the CS radical and than the cosmic isotopic ratio $[^{32}\mathrm{S}]/[^{34}\mathrm{S}] = 22.5$ (Anders & Grevesse 1989).

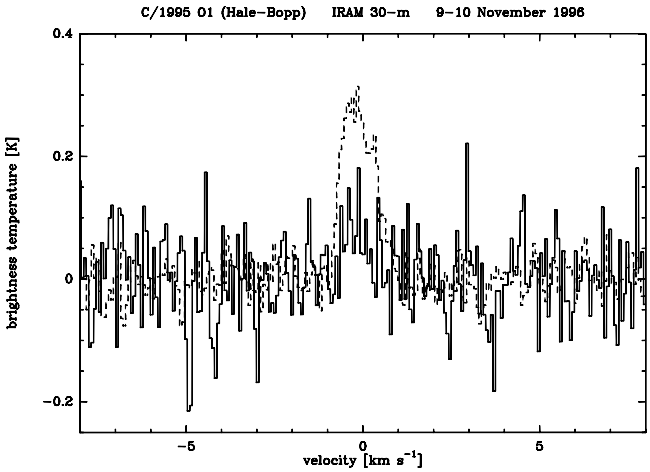

Fig. 4. The $H_2^{34}S$ line observed at IRAM in comet Hale-Bopp (average of 9 and 10 November 1996). The $H_2^{32}S$ line observed on 9 November is shown for comparison in dashes, scaled down by a factor of 5.

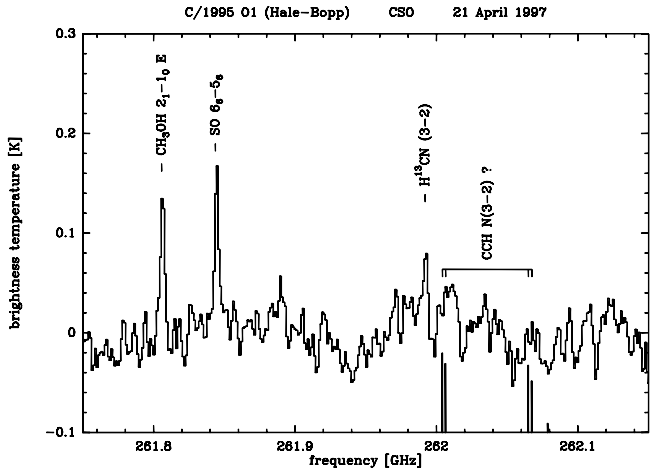

Fig. 5. The C_2H lines tentatively observed at the CSO in comet Hale-Bopp. Bars indicate the relative intensities of the C_2H multiplet. Lines of CH_3OH, SO and $H^{13}CN$ (in the lower sideband) were observed simultaneously.

5. Results: radicals and ions

Many radicals and ions were covered in our survey[3]. Some of them are listed in Table 8:

- SiC (silicon carbide)
- SiO (silicon monoxide)
- HCO radical
- HNO radical
- HCP radical
- $HOCO^+$ (protonated carbon dioxide)
- H_2COH^+ (protonated formaldehyde)
- $HCNH^+$ (protonated hydrogen cyanide)
- N_2H^+ (protonated dinitrogen)

For completeness, we also mention our search for the CH radical lines at 9 cm wavelength performed in May 1997 with the Nançay radio telescope, reported by Crovisier et al. (2002).

These species obviously cannot be parent molecules. We do not provide any evaluation of their upper limits in terms of production rates. Their observations are listed in Table 8. The special case for the C_2H radical is discussed in the next subsection.

5.1. Ethynyl radical (C_2H)

C_2H (ethynyl radical) could be a photo-degradation product of many hydrocarbon species. It could also be responsible for the 2.44 μm unidentified features in infrared spectra of comets (S.J. Kim, *pers. comm.*). Altwegg et al. (1999) suggested the possible presence of C_2H in 1P/Halley coma, from mass spectroscopy, with $Q[C_2H]/Q[H_2O] = 1\text{–}6 \times 10^{-4}$.

[3] Our observations of CN, CO^+, HCO^+ and H_3O^+ are presented and briefly discussed by Lis et al. (1999) and Henry et al. (2001).

Marginal features are present at 262.005 and 262.066 GHz in a CSO spectrum, which also shows features of SO (6_6–5_6), $H^{13}CN$ J(3–2) and methanol (Fig. 5). They might be due to the N(3–2) J(7/2–5/2) and J(5/2–3/2) transitions of this radical. Both features are broader ($\Delta v \approx 15$ km s^{-1}) than other cometary lines. This could be explained by: (i) the hyperfine structure of these multiplet transitions; (ii) the kinematics of C_2H; coming from multi-step photodissociation of hydrocarbons, CH_2 could have higher velocities than parent molecules, when produced with an ejection velocity outside the inner collisional region. The feature corresponding to the N(3–2) J(7/2–5/2) transition is not centred exactly on the expected frequency, however.

We have evaluated the expected signal of C_2H expected from the photodissociation of acetylene. We assumed $Q[C_2H_2] = 0.3\%$ that of water (Dello Russo et al. 2001). C_2H_2 photodissociates preferentially in C_2H with a rate of 10^{-5} s^{-1} at 1 AU (Huebner et al., 1992; Boyé et al., 2002). We assumed that the scale length of C_2H (whose lifetime is unknown) is larger than the instrumental field of view. We derive $\int T_B dv = 150$ and 110 mK km s^{-1} for the N(3–2) J(7/2–5/2) and J(5/2–3/2) blends, respectively. The corresponding features in Fig. 5 are 600 and 200 mK km s^{-1}, respectively. This is a factor two to four larger than expected from the model. However, we consider that the identification is plausible, considering model uncertainties and the expected contributions of C_2H_6 and of still undetected other hydrocarbons to the production of the C_2H radical.

6. Discussion and conclusion

6.1. Methodological issues

From the spectral survey of comet Hale-Bopp at radio wavelengths, the detection of more than 20 molecules, molecular ions, radicals and isotopologues was achieved.

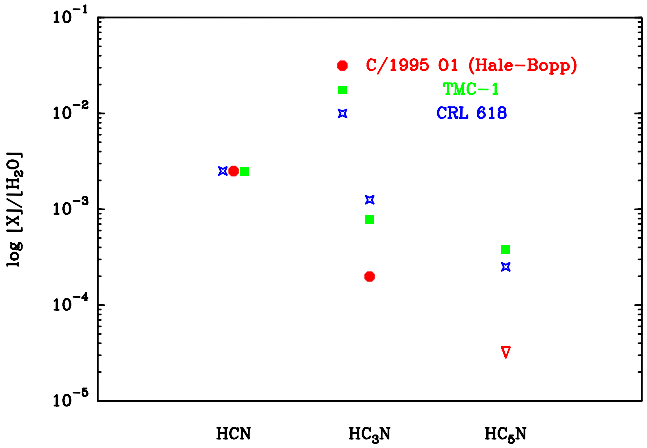

Fig. 6. The relative abundances of linear cyanopolyynes in comet Hale-Bopp (Bockelée-Morvan et al. 2000 and present work), in the dark cloud TMC–1 (Irvine et al. 1987) and in the proto planetary nebula CRL 618 (Cernicharo et al. 2001). For the comet, the abundances are plotted relative to water and the triangle indicates an upper limit. For the interstellar and circumstellar sources, the abundances are normalized to that of HCN.

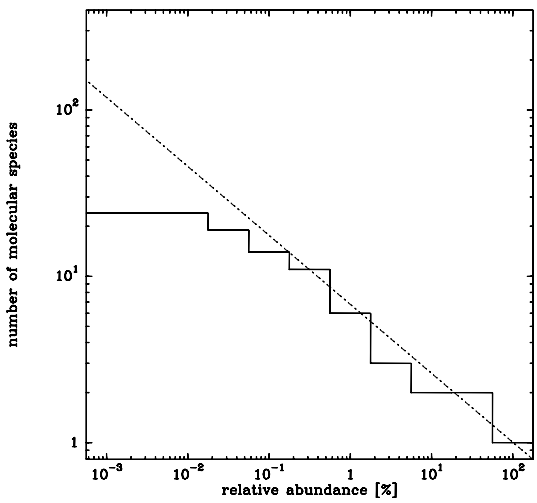

Fig. 7. The number of detected molecular parent species with production rates (relative to water in percent) larger than a given abundance value. The dashed line is a guess of the true distribution.

The present analysis results in setting upper limits on the abundances of ≈ 25 additional molecules and 5 isotopologues (Table 9). The present survey is a significant improvement over those made previously at IRAM on comets C/1989 X1 (Austin) and C/1990 K1 (Levy) (Crovisier et al. 1993), because comet Hale-Bopp had a much higher gas production rate and because of the higher spectral coverage, thanks to the CSO. The improvement over the CSO survey made on comet C/1996 B2 (Hyakutake) (Lis et al. 1997) is not so important in terms of sensitivity (because the close approach of this comet to Earth compensated its more modest gas production rate), but the present survey is more comprehensive because longer observing time could be scheduled.

Table 11. Some unidentified lines observed at the IRAM 30-m telescope

Frequency [MHz]	date dd/mm/yyyy	$\int T_b dv$ [mK km s^{-1}]
96732.7	29/05/1997	42 ± 16
105468.6	03/04/1997	65 ± 21
105551.9	03/04/1997	129 ± 34
106494.8	03/04/1997	54 ± 17
106911.5	03/04/1997	62 ± 16
140782.3	xx/04/1997	180 ± 39
140792.5	03/04/1997	174 ± 39
140794.1	03/04/1997	125 ± 39
146964.3	03/04/1997	75 ± 36
147094.4	03/04/1997	125 ± 31
157014.5	03/04/1997	244 ± 74
203403.0	08/04/1997	203 ± 50
218465.0	03/04/1997	290 ± 60
226777.9	11/04/1997	245 ± 73
227677.6	05/04/1997	137 ± 38
236040.5	04/04/1997	358 ± 68

Some of these features do coincide with molecular lines, but the identifications have been ruled out because the transitions occur between high energy levels, or the same species is expected to have stronger lines that are not seen.

Spectral confusion is still not a problem (in contrast with galactic sources such as Orion or the Galactic Centre): cometary lines are narrow, and rotational temperatures are low. One should remark, however, that in a bright comet such as comet Hale-Bopp, the advantage of the large gas production rate, yielding more intense lines, is in part counterbalanced by the larger expansion velocity and the higher rotational temperature.

The detections are becoming harder when molecular species are getting more complex and heavier. This is easily explained not only because these species are less abundant, but also because their emission is distributed over much more lines (partition function effect), at longer wavelengths. This can be seen from Table 9: very low upper limits could be set to linear species such as NaCl or HC_5N, whereas limits on species such as glycine or dimethyl ether are not stringent.

What is the reliability of our upper limits (Table 9)? To convert column densities into production rates, a parent molecule spatial distribution has been assumed. For secondary species (resulting from chemical processing) or species coming from a distributed source such as organic grains, the listed upper limits are underestimated. For many species, photodissociation rates are lacking (see Table 3). In this case, the default value which is assumed (10^{-4} s^{-1}) corresponds, for the average observing conditions, to a scalelength equal to the instrumental field-of-view radius at a frequency of 135 GHz for the IRAM 30-m, of 270 GHz for the IRAM PdBI, and of 400 GHz for the CSO. It is thus a crucial parameter. As a consequence, upper limits for short-lived species (which therefore "do not fill the beam") may be significantly underestimated.

6.2. Consequences for the chemistry of comets

The present work completes the inventory of molecules in comet Hale-Bopp presented by Bockelée-Morvan et al. (2000). Molecular abundances are rapidly decreasing with increasing complexity. This is clear for the homologous series of linear cyanopolyynes (Fig. 6). This can also be seen from the limit [ethanol]/[methanol] $< 1/25$. The limit [acetic acid]/[formic acid] $< 2/3$ is not so stringent.

This decrease of abundance with increasing complexity is not observed for hydrocarbons: abundances for C_2H_2 and C_2H_6 are not much less than that of CH_4 (Bockelée-Morvan et al. 2004 and references therein). This might be explained by drastic fractionation following condensation/sublimation of this hypervolatile species (Notesco et al. 1997).

6.3. Future prospects

Which molecular species are still to be discovered in comets? 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. Fig. 7 shows the cumulative histogram of the number N of detected species as a function of their abundance X. We have also drawn the power law $N \propto X^{-0.4}$, suggested by the data from the most abundant species. If realistic, this law would imply that observational bias affect species with abundances $< 10^{-3}$, and that we should expect ≈ 100 species with $X > 10^{-5}$.

The presence of unidentified features in cometary spectra already points to the existence of further species. In the visible, many features are noted (e.g., Brown et al. 1996; Cochran & Cochran 2002), presumably due to radicals. Others were recently revealed in the infrared with the Keck/NIRSPEC instrument (Mumma et al. 2001a, 2001b), that could be due to parent molecules. Several unidentified lines at the 3 to 5–σ level of confidence are also noted in our radio survey. Some of them are listed in Table 11.

In the radio domain, future progress will depend upon the apparition of bright, unexpected comets, since there is no short-period comet with high production rate (i.e., $Q[H_2O] > 10^{29}$ s^{-1}) expected in the next years. The emergence of new instruments in the next decade, such as the Atacama Large Millimetre Array, which will provide an increase of sensitivity, or the Herschel Space Observatory, which will open a new spectral range in the submillimetric domain, will certainly contribute new discoveries.

The present work clearly shows the limits of chemical analysis of comets by remote sensing. Really complex species such as amino acids will have to be investigated by space probes with in situ techniques such as gas chromatography, or will need the return to Earth of cometary nucleus samples.

Acknowledgements. We are grateful to all the persons who participated in these target-of-opportunity observations: R. Bachiller, D.J. Benford, J.K. Davies, E. Gérard, B. Germain, M. Houde, D. Mehringer, R. Moreno, G. Paubert, T.G. Phillips, H. Rauer, & J.E. Wink. We thank L.H. Coudert, J. Demaison, E. Herbst, I. Kleiner & G. Wlodarczak who contributed to this work by providing lists of molecular transitions. The JPL and Cologne databases were crucial for the preparation of the observations, quick-look reduction and final analysis. This research has been supported by the Centre national de la recherche scientifique, the Programme national de planétologie de l'Institut national des sciences de l'univers, and NSF grant AST 2209008 to the Caltech Submillimeter Observatory. IRAM is supported by INSU/CNRS (France), MPG (Germany) and IGN (Spain).

References

Altwegg, K, Balsiger, H., & Geiss, J., 1999, Space Scie. Rev., 90, 3

Altwegg, K., & Bockelée-Morvan, D., 2003, Space Scie. Rev., 106, 139

Anders, R., & Grevesse, E. 1998, Geochim. Cosmochim. Acta, 53, 197

Anderson, T., Crownover, R., Herbst, E., & de Lucia, F.C., 1988, ApJS, 67, 135

Bettens, F.L., Sastry, K.V.L.N., Herbst, E., et al., 1999, ApJ, 510, 789

Bird, M.K., Janardhan,P., Wilson, T.L. et al. 1999, Earth Moon Planets, 78, 21

Biver, N., Bockelée-Morvan, D., Colom, P., et al., 1999, Earth Moon Planets, 78, 5

Biver, N., Bockelée-Morvan, D., Crovisier, J., et al., 2002, Earth Moon Planets, 90, 323

Bockelée-Morvan, D., Crovisier, J., Mumma, M.J., & Weaver, H.A., 2004, in: Festou, M., Keller, H.U., Weaver, H.A. (edts) Comets II, Univ. Arizona Press, Tucson, in press

Bockelée-Morvan, D., Gautier, D., Lis, D.C. et al., 1998, Icarus, 133, 147

Bockelée-Morvan, D., Lis, D.C., Wink, J., et al., 2000, A&A, 353, 1101

Bockelée-Morvan, D., Wink, J., Despois, D., et al., 1999, Earth Moon Planets, 78, 67

Boyé, S., Campos, A., Douin, S., et al., 2002, J. Chem. Phys., 115, 3566

Brown, M.E., Bouchez, A.H., Spinrad, A.H., & Johns-Krull, C.M., 1996, AJ, 112, 1197

Canaves, M.V., De Almeida, A.A., Boice, D.C., & Sanzovo, G.C., 2002, Earth Moon Planets, 90, 335

Ceccarelli, C., Loinard, L., Castet, A., Faure, A., & Lefloch, B., 2000, A&A, 362, 1122

Cernicharo, J., Heras, A.M., Tielens, A.G.G.M., et al., 2001. ApJ, 546, L123

Charnley, S.B., Rodgers, S.D., & Ehrenfreund, P., 2001, A&A, 378, 1024

Charnley, S.B., Tielens, A.G.G.M., & Rogers, S.D., 1997, ApJ, 482, L203

Cochran, A.L., & Cochran, W.D., 2002, Icarus, 157, 297

Colom, P., Crovisier, J., Bockelée-Morvan, D., Despois, D., & Paubert, G., 1992, A&A, 264, 270

Colom, P., Gérard, E., Crovisier, J., et al., 1999, Earth Moon Planets, 78, 37

Combes, F., Nguyen-Q-Rieu, & Wlodarczak, G., 1996, A&A, 308, 618

Combi, M.R., Reinard, A.A., Bertaux, J.-L., Quemarais, E., & Mäkinen, T., 2000, Icarus, 144, 191

Coudert, L.H., & Hougen, J.T., 1990, J. Mol. Spect., 139, 259
Cremonese, G., Boehnhardt, H., Crovisier, J., et al., 1997, Ap,J 490, L199
Cremonese, G., Huebner, W.F., Rauer, H.,& Boice, D.C., 2002, Adv. Space Res., 29, 1187
Crifo, J.-F., & Slanina, Z., 1991, ApJ, 383, 351
Cronin, J.R., & Chang, S., 1993, in: Greenberg, J.M., Mendoza-Gomez, C.X., Pirronello, V. (eds) The Chemistry of Life's Origin, Kluwer, Dordrecht, 209
Crovisier, J., 1994, J. Geophys. Res., 99(E2), 3777
Crovisier, J., 1998, Faraday Discuss., 109, 437
Crovisier, J., Bockelée-Morvan, D., Biver, N. et al., 2004, A&A, to be submitted
Crovisier, J., Bockelée-Morvan, D., Colom, P., Despois, D., & Paubert, G., 1993, A&A, 269, 527
Crovisier, J., Colom, P., Gérard, E., Bockelée-Morvan, D., & Bourgois, G., 2002, A&A, 393, 1053
Dello Russo, N., Mumma, M.J., DiSanti, M.J., Magee-Sauer, K., & Novak, R., 2001, Icarus, 155, 163
Despois, D., 1999, Earth Moon Planets, 79,103
Eberhardt, P., Meier, R., Krankowsky, D., & Hodges, R.R., 1994, A&A, 288, 315
Ehrenfreund, P., Berstein, M.P., Dworkin, J.P., Sandford, S.A., & Allamandola, L.J., 2001a, AJ, 550, L95
Ehrenfreund, P., Glavin, D.P., Botta, O., Cooper, G., & Bada, J.L., 2001b, Proc. Nat. Acad. Scie., 98, 2138
Grevesse, N., & Sauval, A.J. 1998, Space Scie. Rev., 85, 161
Groner, P., Albert, S., Herbst, E., & de Lucia, F.C., 1998, ApJ, 500, 1059
Grün, E., Hanner, M.S., Peschke, S.B., et al., 2001, A&A, 377, 1098
Hatchell, J., Roberts, H., & Millar, T.J., 1999, A&A, 346, 227
Helbert, J., Rauer, H., Boice, D., & Huebner, W., 2000, BAAS, 32, 1071
Helminger, P., De Lucia, F.C., & Kirchoff, W.H., 1973, J. Phys. Chem. Ref. Data, 2, 215
Henry, F., Crovisier, J., Bockelée-Morvan, D., Rauer, H., & Lis, D., 2001, Astrophys. Space Scie., 277, 303
Hersant, F., Gautier, D., & Huré, J.-M., 2001, ApJ, 554, 391
Hollis, J.M., Pedelty, J.A., Snyder, L.E., et al., 2003, ApJ, 588, 353
Huebner, W.F., Keady, J.J., & Lyon, S.P., 1992, Astrophys. Space Scie., 195, 1
Ilyushin, V.V., Alekseev, E.A., Dyubko, S.F., et al., 2001, J. Mol. Spect., 205, 286
Ilyushin, V.V., Alekseev, E.A., Dyubko, S.F., & Kleiner, I., 2003, J. Mol. Spect., 220, 170
Irvine, W.M., Dickens, J.E., Lovell, A.J., et al., 1998, Faraday Discus., 109, 475
Irvine, W.M., Dickens, J.E., Lovell, A.J., et al., 1999, Earth Moon Planets, 78, 29
Irvine, W.M., Goldsmith, P.F., & Hjalmarson, Å., 1987, in: Hollenbach, D.J. & Thronson, Jr, H.A. (edts), Interstellar Processes, Reidel Publishing Company, 561
Irvine, W.M., Schloerb, F.P., Crovisier, J., Fegley, B., & Mumma, M.J., 2000a, in: Mannings, V., Boss, A., Russel, S. (eds) Protostars and Planets IV, Univ. of Arizona Press, Tucson, 1159
Irvine, W.M., Senay, M., Lovell, A.J., et al., 2000b, Icarus, 143, 412
Jacq, T., Walmsley, C.M., Mauersberger, R., et al., 1993, A&A, 271, 276
Jewitt, D.C., Matthews, H.E., Owen, T., & Meier, R., 1997, Science, 278, 90
Kleiner, I., Lovas, F.J., & Godefroid, M., 1996, J. Phys. Chem. Ref. Data, 25, 1113
Krasnopolsky, V.A., 1991, A&A, 245, 310
Kuan, Y.-J., Charnely, S.B., Hueng, H.-C., Tseng, W.-L., & Kisiel, Z., 2003, ApJ, 593, 848
Lis, D.C., Keene, J. Young, T.G., et al., 1997, Icarus, 130, 355
Lis, D.C., Mehringer, D., Benford, D., et al., 1999, Earth Moon Planets, 78, 13
Lovas, F.J., Kawashima, Y., Grabow, J.-U., et al., 1995, ApJ, 455, L201
Meier, R., & Owen, T.C., 1999, Space. Scie. Rev., 90, 33
Meier, R., Owen, T.C., Jewitt, D.C., et al., 1998b, Science, 279, 1707
Meier, R., Owen, T.C., Matthews, H.E., et al., 1998a, Science, 279, 842
Miao, Y., Snyder, L.E., Kuan, Y.-J., & Lovas, F.J., 1994, BAAS, 26, 906
Millar, T.J., 2000, in: Wootten, A. (ed.) Science with the Atacama Large Millimeter Array, ASP Conf. Series 235, 45
Müller, H.S.P., Thorwirth, S., Roth, D.A., & Winnewisser, G., 2001, A&A, 370, L49 (electronic files available from `http://www.cdms.de`)
Mumma, M.J., Dello Russo, N., DiSanti, M.A., et al., 2001a, Science, 292, 1334
Mumma, M.J., McLean, I.S., DiSanti, M.A., et al., 2001b, ApJ, 546, 1183
Notesco, G., Laufer, D., & Bar-Nun, A., 1997, Icarus, 125, 471
Nummelin, A., Dickens, J.E., Bergman, P., et al., 1998, A&A, 337, 275
Parise, B., Ceccarelli, C., Tielens, A.G.G.M., et al., 2002, A&A, 393, L49
Pearson, J.C., Sastry, K.V.L.N., Herbst, E., & de Lucia, F.C., 1997, ApJ, 480, 420
Pickett, H.M., Poynter, R.L., Cohen, E.A., et al., 1998, J. Quant. Spect. Rad. Trans., 60, 883 (electronic files available from `http://spec.jpl.nasa.gov`)
Rodgers, S.D., & Charnley, S.B., 2001, MNRAS, 323, 84
Saito, S., Ozeki, H., Ohishi, M., & Yamamoto, T., 2000, ApJ, 535, 227
Scherer, M., Havenith, M., Mauersberger, R.,& Wilson, T.L., 1998, A&A, 335, 1070
Schleicher, D.G., Lederer, S.M., Millis, R.M.,& Farnham, T.L., 1997, Science, 275, 1913
Snyder, L.E., 1997, Origins Life Evol. Biosphere, 27, 115
Weiler, M., Rauer, H., Knollenberg, J., Jorda, L., & Helbert, J. 2003, A&A, 403, 313
Wink, J., Bockelée-Morvan, D., Despois, D., et al. 1999, Earth Moon Planets, 78, 63
Winnewisser, M., & Winnewisser, B.P., 1971, Z. Naturforsch. 26a, 128
Wlodarczak, G., & Demaison, J., 1988, A&A, 192, 313
Woodney, L.M. 2000. PhD thesis, Univ. of Maryland
Woodney, L.M., A'Hearn, M.F., Lisse, C., & McMullin, J., 1999, Earth Moon Planets, 78, 69
Zwart, E., ter Meulen, J.J., Meerts, W.L., & Coudeert, L.H., 1991, J. Mol. Spect., 147, 27