INFRARED OBSERVATIONS OF VOLATILE MOLECULES IN COMET HALE-BOPP

J. Crovisier
Observatoire de Paris-Meudon, F-92195 Meudon, France

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Abstract. Infrared observations of comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) benefited from the high spectral resolution and sensitivity of échelle spectrometers now equipping ground-based telescopes and from the availability of the Infrared Space Observatory (ISO).

From the ground, several hydrocarbons were unambiguously detected for the first time: CH_4, C_2H_2, C_2H_6. Water was observed through several of its hot vibrational bands, escaping telluric absorption. CO, HCN, NH_3 and OCS were also observed, as well as several radicals. This permitted the evaluation of molecular production rates, of rotational temperature, and — taking advantage of the 1-D imaging of long-slit spectroscopy — of the space distribution of these species.

With ISO, carbon dioxide was directly observed for the second time in a comet (after its detection from the Vega probes in P/Halley). The spectrum of water was investigated in detail (several bands of vibration and far-infrared rotational lines), permitting the evaluation of the rotational temperature of water, and of it spin temperature from the ortho-to-para ratio.

Water ice was identified in the grains of Hale-Bopp as far as 7 AU from the ground and possibly at 3 AU with ISO. The composition of cometary volatiles appears to be strikingly similar to that of interstellar ices.

Key words: C/1995 O1 Hale-Bopp, comets, ice, infrared spectroscopy, molecules.

1. Introduction

The infrared domain, which contains all the fundamental bands of vibrations of molecules, is of vital interest for the study of cometary parent molecules. These bands are emitted through fluorescence excited by the solar radiation field (eg. Crovisier 1992). In first approximation, fundamental bands are emitting through resonant fluorescence. Their *total* intensity F observed in a field of view of angular diameter ϕ can be readily converted into column density $< N >$ (except for the strongest bands of water and CO_2 which may be optically thick) through:

$$F = \frac{1}{16} h\nu \frac{g}{r^2} \phi^2 < N > \quad (1)$$

where g is the fluorescence rate of the band at the heliocentric distance $r = 1$ AU. Note that this relation does not depend upon the rotational distribution. Thus the bands do not need to be rotationally resolved, provided they are not blended with other bands. However, if only one (or a few) ro-vibrational line is observed, the rotational distribution must be known to derive the total column density (as for radio observations of single rotational lines); this requires further information.

The best spectral region appears to be between 2.5 and 7 μm, where the bands have the highest fluorescence rates and are less contaminated by thermal emission of cometary dust. The fluorescence rates of vibrational bands are typically of the order of $10^{-5} - 10^{-3}$ s^{-1} at 1 AU from the Sun, which is smaller than the fluorescence rates of the electronic bands of radicals in the visible. Infrared spectroscopy is thus less sensitive to minor species than visible or radio spectroscopy, but still efficient to study the main species. It is in any case the only remote-sensing technique allowing to observe non-polar molecules such as CO_2 and hydrocarbons.

Comets C/1996 B2 (Hyakutake)[1] and C/1995 O1 (Hale-Bopp) were two exceptionally bright comets, the former because it made a close approach to Earth, the later because of its very high outgassing rate.

Comet Hale-Bopp had a gas production rate about ten times higher than P/Halley at the same heliocentric distance. However, its dust production rate was even greater, its gas-to-dust ratio being more than ten times larger than in P/Halley. This implies that the contrast of gas emission bands over dust continuum was very poor. Indeed, near perihelion, gas emission bands could hardly be detected in the infrared at low spectral resolution (Davies et al. 1998; Galdemard et al. 1998). High resolution was required to resolve the vibrational bands and to observe ro-vibrational lines with a high contrast over continuum. Molecules having a small number of lines in their bands (such as linear molecules like CO, HCN, C_2H_2... or symmetric molecules like CH_4, C_2H_6...) were thus more easy to detect than molecules with a *forest* of lines (like CH_3OH).

Due to the novelty of the techniques involved, the pioneering aspect of the investigations, the unexpected character of the discoveries, and last but not least, the hugeness of the data sets which were secured, the results obtained on these two comets are far from being fully exploited. The present review is thus limited to the preliminary results which were revealed at the moment it was made.

[1] Although this Conference is specifically dedicated to comet Hale-Bopp, many outstanding spectroscopic results were obtained on comet Hyakutake, just one year before the perihelion of comet Hale-Bopp. Therefore, we will not dissociate the new results from the two comets.

2. Observations

C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) were the first bright comets whose observations benefited from the dramatic improvement of infrared detectors: the échelle spectrometer CGS4 equipping the United Kingdom Infra Red Telescope (UKIRT) (Davies et al. 1998); the cryogenic échelle spectrometer (CSHELL) on the NASA Infra Red Telescope facility (IRTF) (Mumma et al. 1996; Brooke et al. 1996; Dello Russo et al. 1998; DiSanti et al. 1998; Magee-Sauer et al. 1998; Weaver et al. 1998; Figs 1 and 2) with a spectral resolution $\lambda/\Delta\lambda \approx 20\,000$; the cryogenic grating spectrometer Phoenix on the Kitt Peak 2.2-m telescope (Reuter et al. 1997).

The passage of C/1995 O1 (Hale-Bopp) coincided with the operation of the Infrared Space Observatory (ISO) (Kessler et al. 1996). Unfortunately, this satellite could only observe the comet at $r > 2.9$ AU, because of visibility constraints. Three sequences of observations were performed, at $r = 4.6$ and 2.9 AU pre-perihelion and 3.9 AU post-perihelion (Crovisier et al. 1996, 1997a, 1997b; Leech et al. 1998). A full infrared spectrum of the comet could be secured with a resolution $\lambda/\Delta\lambda \approx 1500$ in the 2.4–45 μm domain and $\lambda/\Delta\lambda \approx 200$ for 44–200 μm.

A wealth of other infrared observations were secured. However, most of them were made with limited spectral resolution or in spectral domains inadequate for the study of gas-phase molecules and are rather relevant to the study of the comet dust (see the review of Hanner et al. 1998).

Table I lists the features observed in infrared spectra of comets with their proposed identifications. One can see that not only most of the features already observed in past comets have been re-observed in Hale-Bopp, but that many new features have been discovered in this comet.

3. Parent Molecules

3.1. Water

Although water is the dominant species among cometary ices, its direct observations are rare because of the difficulty to observe this molecule from the ground. For a long time, the only observations were obtained from space or high altitude, and restricted to the 2.7 μm band (Combes et al. 1988; Mumma et al. 1986; Weaver et al. 1986). The observations of comet Hale-Bopp with ISO, besides the detailed investigation of the 2.7 μm band, resulted in the detections of the ν_2 band at 6.3 μm and of several rotational lines (Crovisier et al. 1997; Leech et al. 1998;

Table I. Molecular bands and lines detected in the infrared spectrum of comets.

λ [μm]	species	band	comet [a]	comments	references [b]
1.10	CN	$A - X(0-0)$	We, P/H	ground	
1.21	C_2	$A - X(0-0)$	We	ground	
1.38	H_2O	$\nu_1 + \nu_3$	P/H	VEGA-TKS	
1.45	C_2	$b - a(2-1)$	We, P/H	ground	
1.46	CN	$A - X(1-2)$	We, P/H	ground	
1.5 [cd]	H_2O ice		H-B	ground	Dav97
1.78	C_2	$b - a(0-0)$	We	ground	
1.94	H_2O	$\nu_1 + \nu_2 + \nu_3 - \nu_1$	P/d'A...	ground	6366, 6374, 6604, Mum96
2.04 [cd]	H_2O ice		H-B	ground	Dav97
2.44	?		We, P/H	ground, unident.	
2.7	H_2O	ν_3 group	P/H, Wi	KAO, VEGA-IKS, ISO	Cro97, Lee98
2.8	H_2O	ν_3...	P/H...	KAO, ground, ISO	Cro97
2.87	OH	$v(1-0)$	H-B	ISO	Cro97
3.0 [cd]	H_2O ice		Bo, C, P/H	ground, ISO, tentative	Lee98
3.00	NH_3	ν_1	H-B	ground	Mag98
3.02	HCN	ν_3	Hyak, H-B	ground	6366, 6573, Bro96, Mag98, Wea98
3.03	C_2H_2	ν_3	Hyak, H-B	ground	6378, 6573, Bro96, Mag98, Wea98
3.04	OH	$v(1-0)$	Hyak	ground	Bro96
3.23	NH_2	ν_1	Hyak	ground	Bro96
3.28	aromatics ?		P/H...		
3.31	CH_4	ν_3	Hyak, H-B	ground	6366, 6374, 6573, Mum96, Wea98
3.3–3.5	X–CH		P/H...	many comets, unident.	
3.35	C_2H_6	ν_7	Hyak, H-B	ground	6366, 6374, 6568, 6573, 6681, Mum96, Wea98
3.35	CH	$v(1-0)$	H-B	ground	6681
3.42	?		P/ST	ground	

Table I. Molecular bands and lines detected in the infrared spectrum of comets (continued).

3.52	CH_3OH	ν_3	P/H...	many comets	6366, 6573
3.59	H_2CO	ν_1, ν_5	P/H	VEGA-IKS tent. ident.	
4.25	CO_2	ν_3	P/H, H-B	VEGA-IKS, ISO	Cro96, Cro97, Lee98
4.63	H_2O	$\nu_3 - \nu_2$	H-B	ground	6604, Wea98
4.67	CO	$v(1-0)$	Hyak, H-B	ground, ISO	6366, 6374, 6568, 6573, Mum96, Cro97, Dis98, Wea98
4.85	H_2O	$\nu_1 - \nu_2$	H-B	ground	6604, 6682, Del98
4.86	OCS	ν_1	H-B	ground	6366, 6681, 6682, Del98
4.90	CN	$v(1-0)$	H-B	ground	6682
6.3	H_2O	ν_2	H-B	ISO	Cro97
6.8	X–OH ?		P/H	KAO, unident.	
9.–12. [c]	silicates		Be...	ground, many comets	
12.2	?		Wi	KAO, unident.	
16. [c]	silicates		H-B	ISO	Cro97
20. [c]	silicates		K...	ground, ISO	
23.5 [c]	silicates		P/H, H-B	KAO, ISO	Cro97
27.5 [c]	silicates		P/H, H-B	KAO, ISO	Cro97
33.5 [c]	silicates		H-B	ISO	Cro97
45. [c]	H_2O ice?		H-B	ISO	Lee98
65. [c]	H_2O ice?		H-B	ISO	Lee98
174.6	H_2O	$3_{03} - 2_{12}$	H-B	ISO	Cro97
179.5	H_2O	$2_{12} - 1_{01}$	H-B	ISO	Cro97

[a] Full designation of comets: Be: C/1969 Y1 (Bennett); K: C/1973 E1 (Kohoutek); W: C/1975 V1 (West); Bo: C/1980 E1 (Bowell); C: C/1983 O1 (Cernis); Wi: C/1986 P1 (Wilson); Hya: C/1996 B2 (Hyakutake); H-B: C/1995 O1 (Hale-Bopp); P/H: 1P/Halley; P/d'A: 6P/d'Arrest; P/ST: 109P/Swift-Tuttle. [b] References are only given for comets Hyakutake and Hale-Bopp. For references to previous comets see Crovisier (1995). Numbers refer to *IAU Circulars*. Bro96: Brooke et al. 1996; Cro96: Crovisier et al. 1996; Cro97: Crovisier et al. 1997a; Dav97: Davies et al. 1997; Del98: Dello Russo et al. 1998; Dis98: DiSanti et al. 1998; Lee98: Leech et al. 1998; Mag98: Magee-Sauer et al. 1998; Mum96: Mumma et al. 1996; Wea98: Weaver et al. 1998. [c] Broad feature. [d] In absorption.

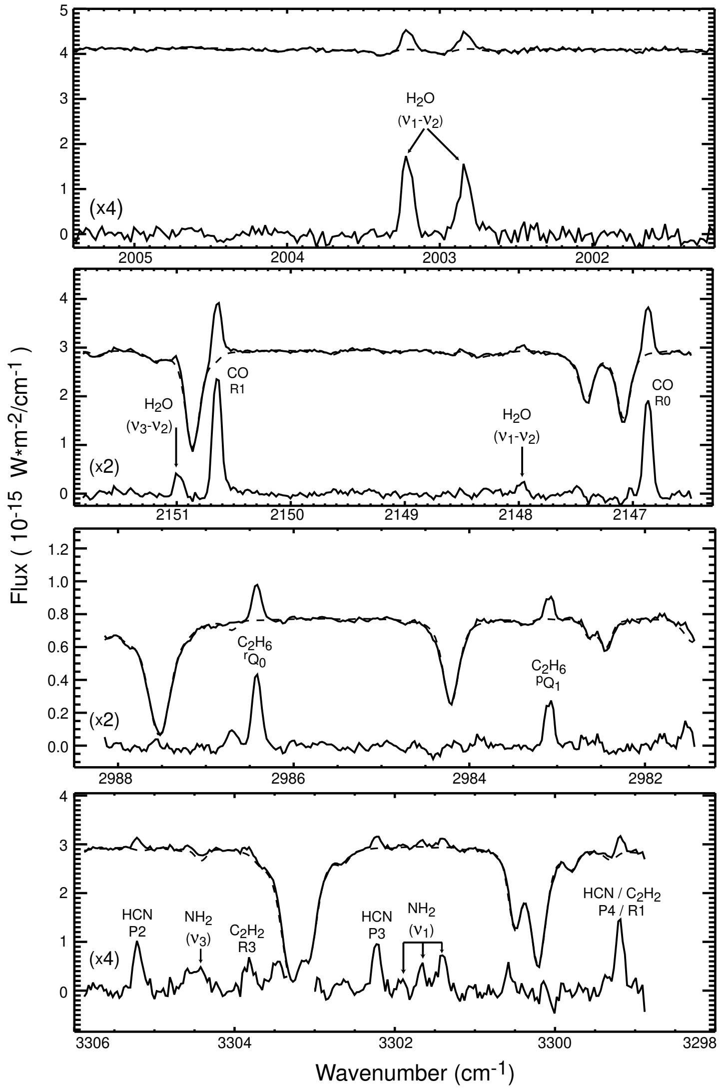

Figure 1. Spectra of C/1995 O1 (Hale-Bopp) obtained on 1.2 May, 1997 (UT) with CSHELL at the NASA-IRTF (solid lines). A comparison with a synthetic atmospheric model (dashed lines) reveals the cometary emissions. The residuals after subtracting the atmospheric model are show at the bottom of each panel (they have been expanded vertically by the factor indicated in the lower left of each panel). The spectra have a resolving power $\nu/\Delta\nu \approx 20\,000$ and the grating was centred at (from top to bottom) 2003 cm^{-1} (Dello Russo et al. 1998); 2149 cm^{-1} (DiSanti et al. 1998); 2985 cm^{-1} (Mumma et al. *in preparation*); 3302 cm^{-1} (Magee-Sauer et al. 1998).

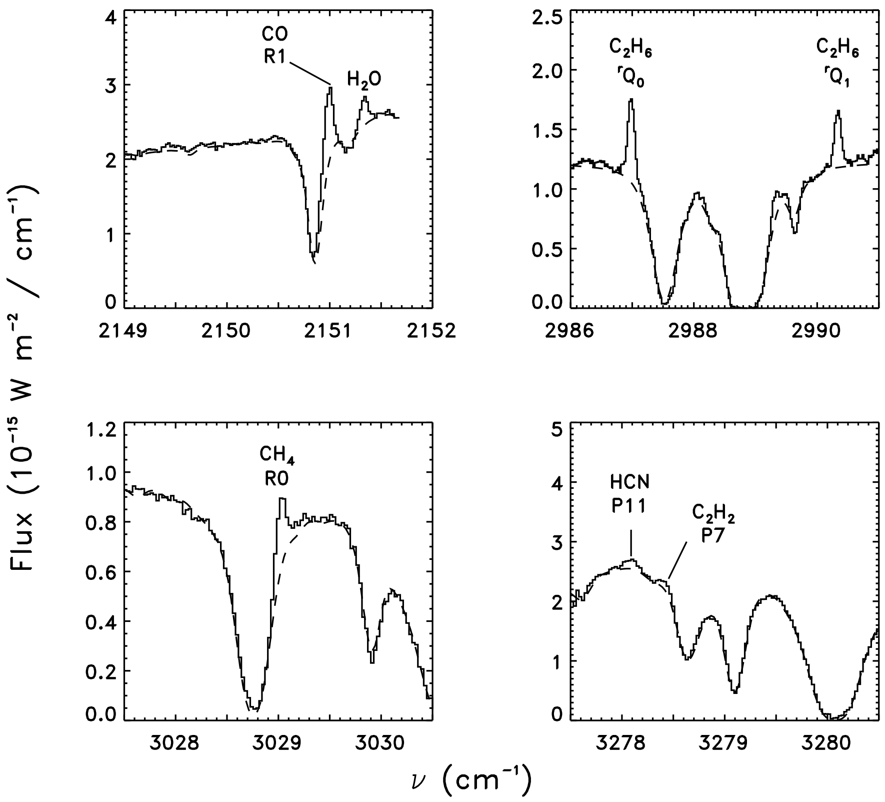

Figure 2. Calibrated spectra showing the lines of CO, H_2O (the $1_{11} - 1_{10}$ line in the $\nu_3 - \nu_2$ band), C_2H_6, CH_4 and C_2H_2, observed in C/1995 O1 (Hale-Bopp) on 2–5 March 1997 with CSHELL at NASA/IRTF. The dashed lines show a model of the cometary continuum including telluric absorption. (From Weaver et al. 1998.)

Figs 3, 4 and 5). With sensitive high-resolution instruments such as IRTF/CSHELL, however, appeared the possibility to observe several hot bands ($\nu_1 - \nu_2$, $\nu_3 - \nu_2$, $\nu_1 + \nu_2 + \nu_3 - \nu_1$) and even some lines of the ν_1 main band from the ground.

The scheme of the fluorescence cascades within the vibrational states of water is shown in Fig. 3.1. Quite promising is the possibility to observe the $\nu_1 + \nu_2 + \nu_3 - \nu_1$ band at 1.94 μm, first revealed in comets 6P/d'Arrest and Shoemaker-Levy 1992 XIX (Mumma et al. 1995), and now observed in comets Hyakutake and Hale-Bopp (Mumma et al. 1996; Dello Russo et al. 1998). Retrieving water production rates from this band, however, is difficult because the line strength of this hot band (and therefore its fluorescence rate), not observed in the laboratory, is unknown. Assuming the same strength for this band as for the corresponding cold band (ν_1) lead to estimations of production rates that made sense (Mumma et al. 1996), but a precise calibration of the method is definitely needed. More generally, now that several hot bands of water are observed (e.g. Fig. 4), a full modelling of the fluorescence cascade of water is required (Fig. 3.1).

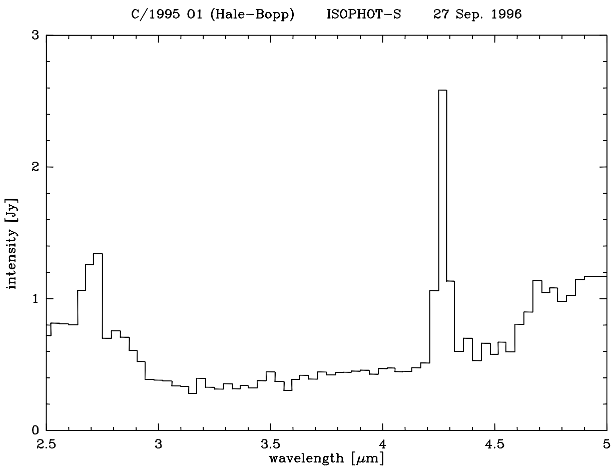

Figure 3. The 2.5 to 5 μm spectrum of C/1995 O1 (Hale-Bopp) observed with the PHT-S instrument of ISO on 27 September 1996. The bands of H_2O at 2.6 μm, CO_2 at 4.25 μm and CO at 4.65 μm can be seen (from Crovisier et al. 1997a).

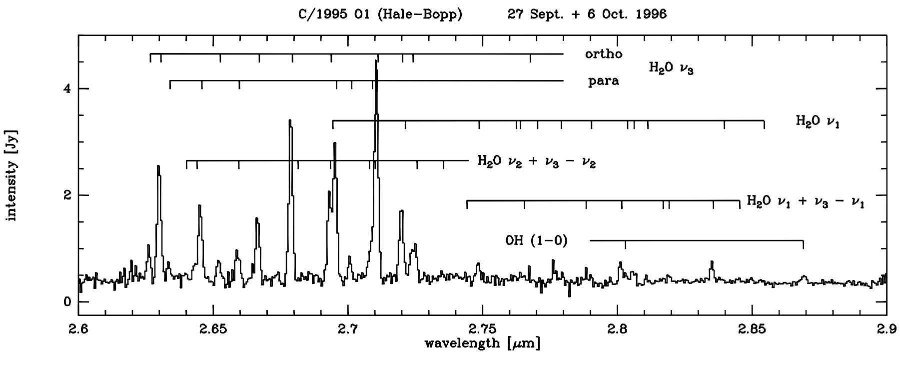

Figure 4. The region of the ν_3 band of water observed in C/1995 O1 (Hale-Bopp) on 26 September and 6 October 1996 with the ISO short wavelength spectrometer, with line assignations (from Crovisier et al. 1997b).

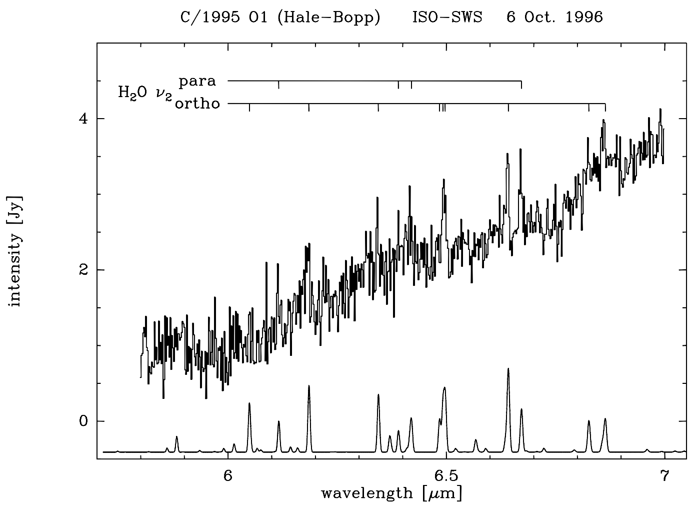

Figure 5. The ν_2 band of water (top) observed in C/1995 O1 (Hale-Bopp) on 6 October 1996 with the ISO short wavelength spectrometer, with line assignations and a synthetic spectrum of water computed for T_{rot} = 28 K (bottom) (from Crovisier et al. 1997b).

3.2. Carbon dioxide

Carbon dioxide definitely cannot be observed from the ground. It was previously observed only once in a comet, in P/Halley with the infrared spectrometer aboard the VEGA space probe (Combes et al. 1988). CO_2 can be indirectly traced from prompt emission of the CO Cameron bands in the UV following CO_2 photodissociation (e.g. Weaver et al. 1997b), but CO_2 production rates cannot be reliably derived from these observations because the rates of the relevant mechanisms are ill known.

ISO could observe the ν_3 band of CO_2 at three moments (Crovisier et al. 1997a; Leech et al. 1998; Fig. 3). These measurements confirmed that CO_2 is a major constituent of cometary volatiles, with a production rate at large heliocentric distances that could exceed that of water, and which is about one third that of CO. For instance, H_2O:CO:CO_2 was 100:70:22 at r = 2.9 AU, and 100:500:110 at r = 3.9 AU. This might indicate that the sublimation of CO_2 is linked to apolar volatiles such as CO, rather than to water.

3.3. Hydrocarbons and other species

One of the major results of the investigations of comets Hyakutake and Hale-Bopp is undoubtedly the definite identifications of three hydro-

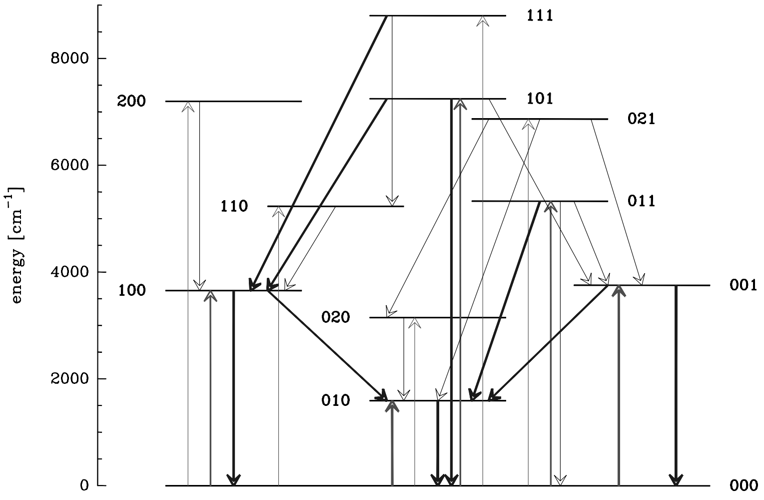

Figure 6. The lower vibrational levels of water and the fluorescence cascade following solar excitation. Detected bands are shown by thick arrows. Several weak bands are omitted.

carbons: methane, acetylene and ethane (Brooke et al. 1996; Mumma et al. 1996; Magee-Sauer et al. 1998; Weaver et al. 1998) (Figs 1 and 2). With preliminary abundances relative to water of 0.6, 0.5 and 0.1 per cent for CH_4, C_2H_6 and C_2H_2, respectively (Weaver et al. 1998), these molecules are major cometary volatiles. The high abundance ratios of C_2H_2 and C_2H_6 relative to CH_4 confirm that cometary ices were formed through out-of-equilibrium chemistry such as that which governed the formation of interstellar molecules. They also suggest that more complex hydrocarbons may still exist in cometary ices. The amounts of C_2H_2 and C_2H_6 are sufficient, in principle, to explain the abundance of the C_2 cometary radical observed in the visible, thus giving an answer to a very old question (one of the first species observed in cometary spectra, C_2 has been an *orphan molecule* for more than a century!).

The detections of ro-vibrational lines of other species: CO, HCN, OCS, NH_3 (Brooke et al. 1996; Mumma et al. 1996; Dello Russo et al. 1998; DiSanti et al. 1998; Weaver et al. 1998) came as no surprise, since these molecules were already known from radio and UV (for CO) observations. However, infrared observations are revealing additional informations on the spatial extent, production rates, modes of production and rotational temperatures of these species (see Section 5). In addition to the species mentioned above, several other species were unsuccessfully searched for.

3.4. The 3.2–3.6 μm emission band

The discovery of a strong emission band at 3.2–3.6 μm was one of the most important outcomes of the observing campaign of P/Halley. The origin of this band was mysterious for some time. It corresponds to the stretching mode of C–H in carbonaceous molecules, but fluorescence of gas-phase molecules and thermal emission of organic grains seemed then to be two equally possible mechanisms. After radio and infrared observations of methanol in C/1989 X1 (Austin), it was found out that this species can account for a large part of this emission, but not for all of it (see review of Bockelée-Morvan et al. 1995 and references therein).

Observations of the 3.2–3.6 μm band as a whole in comet Hale-Bopp were difficult. Far from the Sun, this band (presumably emitted by fluorescence) was weak and barely detected either from space (ISO; Crovisier et al. 1997a) or from the ground (UKIRT; Davies et al. 1998). Near perihelion, as stated above, it was overwhelmed by the strong thermal emission of dust. Only the sharp Q branch of the ν_3 band of methanol was reported.

Infrared high-resolution spectroscopy, however, has identified molecules in significant abundance that undoubtedly contribute to this emission band: CH_4 and C_2H_6. (Other species such as CH_3CN, HCOOH and other, which were identified by their radio lines, also have bands in this spectral range, but their abundances are much smaller and their contribution to the emission is very small.)

The presence of CH_4, C_2H_2 and C_2H_6 is strongly suggesting the existence of many additional hydrocarbons, all of them having vibrational bands in this spectral range. It thus seems now highly likely that all the 3.2–3.6 μm emission band could be due to the fluorescence of such gas-phase molecules, without invoking other exotic species or emission mechanisms from the organic mantle of dust grains. Part of the answer to the nature of the lacking species is perhaps in the identification of the unidentified infrared features (see next Section). A prominent sharp feature at 3.425 μm was observed in 109P/Swift-Tuttle (DiSanti et al. 1995). Whether this feature is also present in Hale-Bopp and what is its origin are still open questions.

To our knowledge, the recent observations have not brought any new clue to the issue of the possible presence of polycyclic aromatic hydrocarbons (PAHs) in cometary material. The 3.28 μm feature, characteristic of aromatics and already noticed in several comets, has not been reported in ground-based spectra of Hale-Bopp, even around perihelion. Although ISO observations have confirmed that PAHs are a ubiquitous component of cosmic matter, ISO spectra of Hale-Bopp have not revealed any feature of PAHs. The 9–12 μm region is dominated by the very strong silicate feature without any sign of the 12 μm PAHs band. The 6.2, 7.7 and 8.6 μm PAHs bands are undetected (the only spectral feature observed in this spectral region is the ν_2 band of water; Fig. 5). The 3.2–3.6 μm band is barely detected with no sign of the 3.28 μm aromatic feature. However, all ISO observations of the comet were done at $r > 2.9$ AU, where the temperatures of the nucleus and of dust grains are unlikely to be high enough to permit the sublimation of PAHs.

4. Radicals and Unidentified Lines

Many radicals are present in the infrared spectrum of comets (Table I). They appear from their vibrational bands (OH, CH, CN, NH_2) or, in the near infrared, from electronic systems (CN, C_2). Their observation could usefully complete the study of the excitation of these species. It should be noted that the C_2 $a - X$ intercombination transitions around 2 μm have been looked for, but were not detected (Rousselot et al. 1998).

Unidentified features in the infrared spectra of comets have been noted in several occasions in the past (Table I). Many additional ones are present in the IRTF/CSHELL spectra. It is unlikely that these features correspond to simple molecules, which have well known spectra. They might be due to more complex species or to radicals.

5. Investigating Physical Conditions

5.1. Spatial distribution

The 1-D mapping capability of the long slit spectrometer of IRTF/CSHELL and its good angular resolution (1×2 arcsec) have been used to investigate the spatial distribution of molecules (Fig. 7). This is a powerful means to distinguish between parent molecules really coming from the nucleus and molecules coming from a distributed source. A preliminary analysis suggests that CO (DiSanti et al. 1998; Weaver et al. 1998) and even H_2O and OCS (Dello Russo et al. 1998) could have an extended origin. The most compelling case seems to

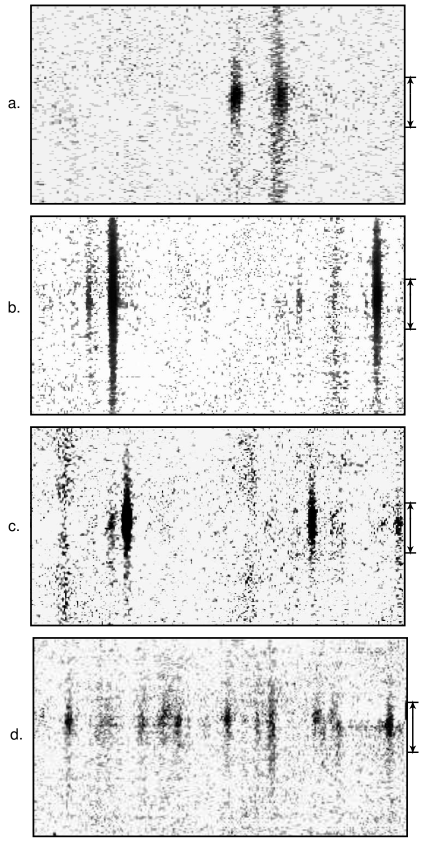

Figure 7. Spatial-spectral images of C/1995 O1 (Hale-Bopp) corresponding to the CSHELL NASA-IRTF spectra shown in Fig. 1. The spatial dimension is vertical and the spectral dispersion is horizontal. For each spectral image, the cometary continuum emission has been subtracted to better reveal the cometary molecular emission lines. The spatial extend of each panel is approximately 30 arcsec on the sky and the length of the arrows shown to the right represent 10 000 km at the comet. Note the larger spatial extend of the CO lines in panel b, compared to the other lines.

be that of CO. These interpretations, however, require a careful subtraction of continuum, an assessment of the tracking accuracy, and an investigation of opacity effects, of possible variations in the activity of the comet, and of the variation of the excitation conditions as a function of distance to nucleus. These issues have not all been considered at the present time. It will be interesting to compare these results with the interferometric mapping at similar spatial resolutions of radio lines of CO and other *parent* molecules (Wink et al. 1998).

5.2. Rotational temperature

High-resolution spectroscopy allows us to sample the rotational distribution of cometary molecules and therefore to study the physical conditions within the coma. By sampling smaller regions, infrared spectroscopy is sensitive to a region closer to nucleus than single-dish radio telescopes (about 1 arcsec to be compared with 10–20 arcsec), where local thermal equilibrium is likely. Observing the rotational temperature as a function of distance to the nucleus is a powerful test of hydrodynamical models of the cometary atmosphere. Temperatures of the order of 100 K were observed in the central region from the lines of HCN and CO for comet Hale-Bopp near perihelion (DiSanti et al. 1998; Magee-Sauer et al. 1998) and the temperature was found to increase with distance to the nucleus. In contrast, the rotational temperature observed by ISO for the ν_3 band of water was 28 K at 2.9 AU from the Sun, in a 14×20 arcsec field of view (Crovisier et al. 1997a).

5.3. Ortho-to-para ratios

Molecules with hydrogen atoms at symmetrical positions may exist in different nuclear-spin species according to the relative orientations of the spins of their H-atoms. These species are called *ortho* and *para* for molecules with two H-atoms like H_2, H_2O or H_2CO, A and E for molecules with three H-atoms like NH_3 or CH_3OH, A, E and F for CH_4, and so forth. Conversions between different species, either by radiative transition or by collisions, are strictly forbidden, at least in the gas phase, and presumably very slow (by proton-exchange mechanisms) in the solid phase. Therefore, the *ortho*-to-*para* ratio (*OPR*) (or E/A ratio) of the molecular rotational distribution may be characteristic of the formation conditions of the molecules (Crovisier 1984; Mumma et al. 1987).

First attempts have been made to evaluate the *OPR* of water from the Kuiper Airborne Observatory (KAO) observations of comets 1P/Halley and C/1986 P1 (Wilson) (Mumma et al. 1988). For comet Halley, an *OPR* of 2.5 ± 0.1 was claimed, smaller than the limit value of 3 and corresponding to a spin temperature of 29 K; a value 3.2 ± 0.2 was found for comet Wilson, consistent with $T_{spin} > 50$ K (Mumma et al. 1993). These results are controversial, however, because retrieving the rotational population distributions from the KAO is model-dependent (Bockelée-Morvan and Crovisier 1990).

A high-resolution spectrum of the whole ν_3 band of water was observed in comet C/1995 O1 (Hale-Bopp) with ISO (Fig. 4). The retrieved *OPR*, taking into account opacity effects (as modelled by

Bockelée-Morvan 1987), is 2.45 ± 0.10 and corresponds to a spin temperature of 25 K (Crovisier et al. 1997a). One could wonder about the meaning of such a temperature. It could be the formation temperature of water, thus excluding formation in a warm Solar Nebula. But chemical reactions leading to the formation of water are exothermal and should produce *hot* (i.e. $OPR = 3.0$) water; it would be interesting to know what is the spin temperature of interstellar water. The possibility of re-equilibration in the nucleus during the long storage time in the Oort's cloud, however, should also be investigated.

Other spin temperatures could, in principle; be derived from infrared observations of other species such as CH_4, C_2H_2, C_2H_6 or NH_3. The species the most sensitive to temperature appear to be CH_4 and NH_3. For the A-to-F ratio of CH_4 observed in comet Hyakutake, Weaver et al. (1997a) found no difference from the high-temperature limit and put a lower limit of 50 K to the spin temperature. They pointed out that methane could re-equilibrate at the moment of sublimation.

6. The Composition of Cometary and Interstellar Ices

6.1. Icy grains in comet Hale-Bopp

The presence of icy grains in cometary atmospheres and their role in outgassing is attested by the observation of water at large heliocentric distances and by the variation of its production with r, for which outgassing from superheated icy grains has been invoked (Biver et al. 1997). Icy grains are not easy to observe because of their very short life time at small r's and no convincing direct observations could be provided in the past (from the 3-μm feature, see Table I).

Davies et al. (1997) claimed the detection of icy grains in comet Hale-Bopp at $r = 7$ AU, soon after its discovery, from absorption features over solar reflected continuum at 1.5 and 2.04 μm (Fig. 8). However, the same features could not be retrieved in subsequent observations by Davies et al. (1998) when the comet was at ≈ 4 AU. Water ice is also identified in the ISO spectra observed at $r \approx 3$ AU, from features in emission at 45 and 65 μm and tentatively in absorption around 3.1 μm (Leech et al. 1998).

Other clues from the presence of icy grains come from broadband imaging in the near infrared and visible (Tozzi et al. 1998; McCarthy et al. 1998). The presence of icy grains may of course be related with the extension of water suspected from IRTF observations (Dello Russo et al. 1998; see above).

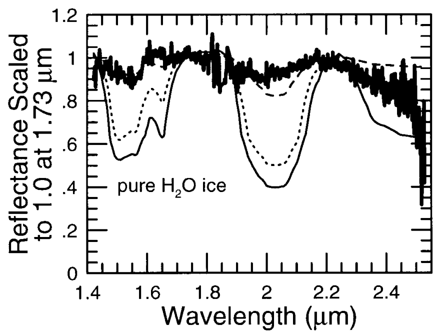

Figure 8. The 1.4–2.5 μm spectrum of C/1995 O1 (Hale-Bopp) observed at 7 AU from the Sun at UKIRT (heavy solid line). The broad absorption bands at 1.5 and 2.05 μm are attributed to water ice. The dashed, dotted and thin solid lines show reflectance spectra of water ice grains of various diameters. (From Davies et al. 1997.)

6.2. Comparison of cometary and ISM ices

No single technique can provide a complete view of the composition of cometary ices. It can only be established from a compendium of the results of radio, infrared and ultraviolet spectroscopy. Summaries of the volatile abundances in comet Hale-Bopp have been shown in this Conference and published elsewhere (e.g. Bockelée-Morvan and Crovisier 1997; Despois 1998): they will not be reproduced here. Most of the abundance values available at the present time are still preliminary and will have to be updated in the future as the observational results are published and analyzed.

The comparison of cometary and interstellar ices is of primary importance to understand the origin and history of comets. (For recent reviews on this topic, see Crovisier (1998a, 1998b), Ehrenfreund et al. (1997), Mumma et al. (1993) and Mumma (1997).)

The composition of ices in interstellar medium (ISM) clouds is known by observing the infrared absorption spectrum of deeply embedded protostars. This is a way of investigation completely different from that of cometary ices, which are known from the fluorescence spectrum of their sublimation products. Here again, ISO observations have completely renewed our knowledge of ISM ices with the observations of interstellar ices towards sources such as RAFGL 7009 (d'Hendecourt et al. 1996) and NGC 7538/IRS9 (Whittet et al. 1996).

Table II. Comparison of the abundances of ices in the interstellar medium (towards IRS9) and of cometary volatiles (at $r \sim 1$ AU). Cometary abundances are from Bockelée-Morvan and Crovisier (1997). ISM ice abundances are taken from a compilation of Schutte (1998) from various sources as well as from recent ISO results (Ehrenfreund et al. 1997; Whittet et al. 1996).

species	interstellar ices		cometary volatiles	
H_2O	= 100		= 100	
CO	10–40		20	
CH_3OH	5		2	
CO_2	10		6	
H_2CO	2–6	tentative	~ 1	
HCOOH	3	tentative	0.05	
CH_4	1–2		~ 1	
other hydrocarbons	?		~ 1	C_2H_2, C_2H_6
NH_3	< 10		0.6	
O_3	≤ 2		?	
X–CN	$\leq 0.5 - 10$		0.37	nitriles + HNCO
OCS, XCS	0.2		0.7	OCS + CS
SO_2	?		~ 0.15	
H_2	$>\sim 1$		?	
N_2	?		?	
O_2	?		?	

Table II shows a comparison of the volatile abundances observed in Hale-Bopp (as compiled by Bockelée-Morvan and Crovisier 1997) and in interstellar ices (from Ehrenfreund et al. 1997, Schutte 1998 and Whittet et al. 1996). The cometary abundances must be considered with some caution, since they may not reflect exactly the original composition of ices due to chemical fractionation processes inside the nucleus as it is heated by the Sun. However, the comparison of the compositions of the two types of objects is compelling: the major constituents in both kinds of objects — H_2O, CO, CO_2, CH_3OH, H_2CO, CH_4 — have the same relative abundances within a reasonable factor. The discrepancies (e.g. for HCOOH) or the non-detection of some cometary molecules in interstellar ices (e.g. for C_2H_2 or C_2H_6) concern minor species. They may be fully accounted for by the smaller sensitivity of the investigations of interstellar ices. A limit of 0.4 % has been put to the abundance of ethane relative to water, however, has been put to NGC 7538/IRS9 (Boudin et al. 1998): this is close to the abundances observed in Hyakutake and Hale-Bopp.

7. Conclusion

Infrared spectroscopy is a major technique for studying cometary volatiles. Its investigations of comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) permitted

- to observe many volatiles, especially H_2O, CO_2, and hydrocarbons CH_4, C_2H_2 and C_2H_2, inaccessible to other techniques;
- to determine the rotational temperatures of these species, thus probing the physical conditions within the cometary atmosphere;
- to determine their space distribution, probing whether they are coming from the nucleus or from extended sources;
- to measure the spin temperature of water, a tracer of cometary origins;
- to reveal the features of still unidentified species.

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