Hunt for Molecules
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HUNT FOR MOLECULES IN COMETS

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Abstract. First cometary spectra were obtained in the middle of the nineteenth century in visible light. They revealed secondary products present in cometary atmospheres. Many parent molecules subliming from the nuclear ices are now identified, most of them at infrared and radio wavelengths. We summarize the hunt for cometary molecules using a chronological approach.

1 Introduction

The molecular and isotopic composition of cometary ices provides key information on the chemical and physical properties of the outer solar nebula where comets formed 4.6 Gyr ago. Our present knowledge on comet chemistry comes mainly from remote sensing spectroscopic observations of cometary atmospheres from space or ground-based telescopes, though key informations were clearly obtained from in situ measurements in the coma of 1P/Halley.

Up to the mid 80s, cometary spectra were essentially obtained at optical and UV wavelengths and revealed signatures of radicals and ions formed by the photodissociation and photoionisation of parent molecules subliming from nuclear ices. Electronic bands of parent molecules generally fall in the UV domain. Their electronic states usually predissociate so that absorption of UV solar photons leads to their destruction rather than to fluorescence. Therefore, the hunt for parent molecules in comets from remote sensing observations really began when sensitive instrumentation in the infrared and

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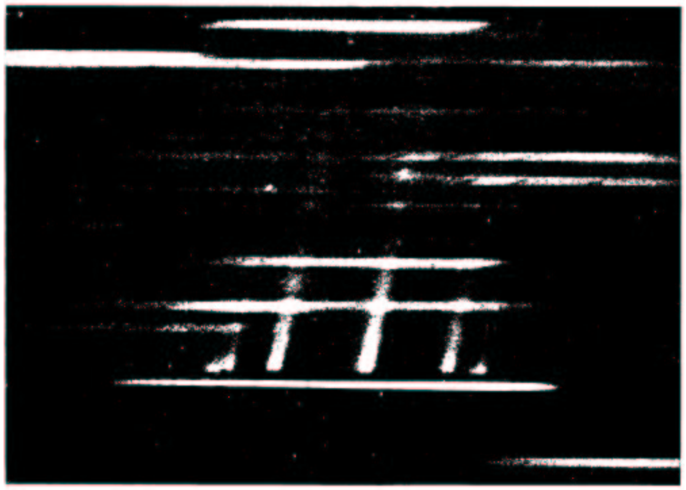
millimetric domains was made available. Most parent molecules have strong fundamental bands of vibration in the 2.5–5 μm where there is abundant solar flux for exciting infrared fluorescence. Millimetre and submillimetre spectroscopy is also powerful to detect parent molecules through their rotational transitions, because of the cold environment (coma temperatures of typically 40–100K) and radiative excitation which leads generally to cold rotational temperatures.

In this paper, we summarize spectroscopic investigations of comet composition using an historical perspective. On purpose, we mainly show historical spectra. Several reviews on the topic were already published. We invite the reader to read for example the chapters of Feldman et al. (2004) and Bockelée-Morvan et al. (2004) in the Comets II book (University of Arizona Press) for detailed reviews and bibliography concerning photo-products, and parent molecules, respectively. Several chapters in that book focus on cosmogonic implications, not discussed here.

2 The hunt for molecules in comets

2.1 Hunt in the visible and UV windows

The hunt for molecules in comets began about 140 years ago (see the review of Swings 1965). The first spectrum of a comet was observed visually by Giovanni Donati on August 5, 1864 on comet C/1864 N1 (Tempel). Sir William Huggins compared the spectrum of comet C/1868 L1 (Winnecke) with flame spectra and found the same bands that he was able to assign to the Swan (C_2) bands, also called "carbon bands". Four bright comets made spectacular apparitions in the years 1881–1882, and not less than 80 papers were published on the spectra of these comets. Photographic plates were becoming available. Huggin's photographed spectrogram of the Great Comet C/1881 K1 revealed CN, C_3, CH and Na-D emission lines. De la Baume Pluvinel and Baldet extensively observed comets with an especially developed objective prism spectrogram and identified CO^+ lines in comet C/1908 R1 (Morehouse). Figure 1 shows the historical spectrum of comet Morehouse between 4000 and 6000 Å where C_2, CO^+, and CN bands are present. In 1941, the OH 3090 Å and NH 3360Å emissions were identified in spectra of C/1940 R2 (Cunningham). A composite 3000-9500 Å low-resolution spectrum of comet 109P/Swift-Tuttle obtained in 1992 is shown in Fig. 2. This spectrum is typical of the head of comets in the inner Solar



THE SPECTRUM OF COMET MOREHOUSE
Photographed with 60° objective-prism on October 18, 1908, with exposure of 3h 57m
Enlarged 4.7 times from the original negative

Fig. 1. The 3000-6000 Å spectrum of comet Morehouse showing the CN violet system (3883 Å), three bands of the comet-tail CO^+ system (4000 to 4600 Å) and C_2 Swan (4737 Å) band (De la Baume Pluvinel & Baldet 1911).

System. In addition to CN, CH, NH, C_2, C_3 and OH signatures, bands from NH_2 and the $O(^1D)$ forbidden transition are present. Visible spectra of comet tails show various molecular ions (CH^+, CO^+, CO_2^+, H_2O^+, N_2^+, and OH^+, Table 1).

First UV observations of comets performed in the 1970s by Earth orbiting spacecrafts led to the discovery of large Lyman-α halos of neutral atomic hydrogen around comets. Rocket spectra of comet C/1975 V1 (West) showed for the first time ultraviolet emission from CS (2576 Å) and CO (1500 Å). The ultraviolet spectrum of comets was extensively observed by the International Ultraviolet Explorer (IUE) in the 1978–1996 period from which emissions of OH, H, O, CO, CO_2^+, C, CS and S were analysed. UV investigations continued with the Hubble Space Telescope, with the important discovery of S_2 emission near 2900 Å in comet C/1983 H1 (IRAS-Araki-

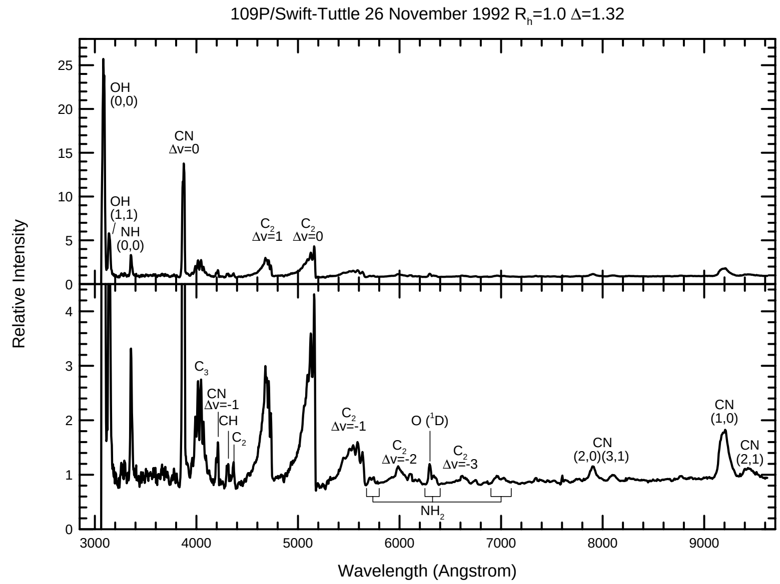


Fig. 2. Composite spectrum of comet 109P/Swift-Tuttle obtained November 26, 1992 (from Feldman et al. 2004).

Alcock). More recently, observations with the Far Ultraviolet Spectroscopic Explorer (FUSE) revealed lines of H_2 in comet C/2001 A2 (LINEAR).

Among all species detected in the optical and UV cometary spectra, only CO and S_2 are presumably released from cometary ices (Table 2). H_2 is, as OH, H and O, a secondary species produced by the photodissociation of water. Possibly PAHs signatures (phenanthrene and pyrene) were identified in 1P/Halley UV spectra obtained by the TKS experiment onboard Vega spacecraft, but this is debated and would demand confirmation. Hundreds of lines remain to be identified in high-resolution cometary UV/visible spectra. Table 1 lists all secondary species detected in cometary spectra (including in the radio range).

radicals	OH, CH, NH, NH_2 CN, C_2, C_3, CS, NS, SO $C^{34}S$, ^{13}CN, ^{13}CC,$C^{15}N$
atoms	H, C, O, S Na, K*, Ca*, Cr*, Mn* Fe*, Ni*, Cu*, Co*, V*
molecular ions	H_2O^+, H_3O^+, OH^+ CO^+, CO_2^+, HCO^+ CH^+, N_2^+
atomic ions	O^+, C^+ Ca^{+*}

Table 1. Radicals, Atoms, and Ions in Comets detected by spectroscopy. Asterisks indicate species only detected in sungrazing comets.

2.2 Hunt in the infrared window

The infrared spectral region has been a rich source of molecular identifications in cometary comae. The first species detected was H_2O, from high resolution spectra of its 2.7 μm fundamental band obtained in comet Halley from the Kuiper Airbone Observatory (Table 2). The entire 2.5–5 μm region was explored at modest resolution by the Infra Krasnoe Spectrometre (IKS) instrument onboard the Vega 1 probe to comet Halley (Combes et al. 1986). Besides H_2O detection, this spectrum revealed organic species through their CH streching modes in the 3.2–3.6 μm region, the presence of CO_2, a tentative detection of H_2CO and marginal signatures of OCS and CO (Fig. 3). The advent of sensitive, high dispersion spectrometers at the NASA Infrared Telescope Facility and Keck telescopes allowed resolution of the rotational structure of the vibrational bands, which is crucial for unambiguously identifying molecules in the spectrally confused 3.2–3.6 μm region. In 1990, CH_3OH was identified as responsible for the 3.52 μm feature observed in several IR spectra, soon after its detection at millimetre wavelengths. In 1996, CH_4, C_2H_2 and C_2H_6 were identified in comet C/1996 B2 (Hyakutake) which made a spectacular apparition due to close approach to Earth. These species as well as HCN, CO, NH_2, hot bands of water and OH prompt emission are now routinely observed in the infrared. Numerous unidentified ro-vibrational lines are observed between 3.2–3.6 μm, but this

Year	Comet	Technique
1976	*C/1975 V1 (West)*	
	CO	UV
1983	*C/1983 H1 (IRAS-Araki-Alcock)*	
	S_2	UV
	NH_3 ?	radio
1985-1986	*1P/Halley*	
	H_2O, CO_2	IR
	HCN	radio
	H_2CO ?, OCS ?	radio, IR
	$C_{14}H_{10}$?	UV
1990	*C/1989 X1 (Austin), C/1990 K1 (Levy)*	
	H_2CO, H_2S	radio
	CH_3OH	radio, IR
1996	*C/1996 B2 (Hyakutake)*	
	NH_3, HNC, CH_3CN, OCS?, HNCO?	radio
	CH_4, C_2H_2, C_2H_6	IR
	HDO, $H^{13}CN$	radio
1997	*C/1995 O1 (Hale-Bopp)*	
	HNCO, HC_3N, OCS, SO_2, H_2CS	radio
	NH_2CHO, HCOOH, $HCOOCH_3$, CH_3CHO	radio
	$HOCH_2CH_2OH$ (*identified in 2003*)	radio
	$HC^{15}N$, DCN, $H_2^{34}S$	radio

Table 2. Chronology of identification of parent molecules in comets. Question marks indicate tentative or debated detections.

region is polluted by several bands of CH_3OH which rotational structures are not yet available.

2.3 Hunt in the radio window

The first definite detection of cometary radio emission was that of the 18-cm transitions of OH in comet C/1973 E1 (Kohoutek) using the Nançay radio telescope (Fig. 4). Since then, more than 80 comet apparitions were

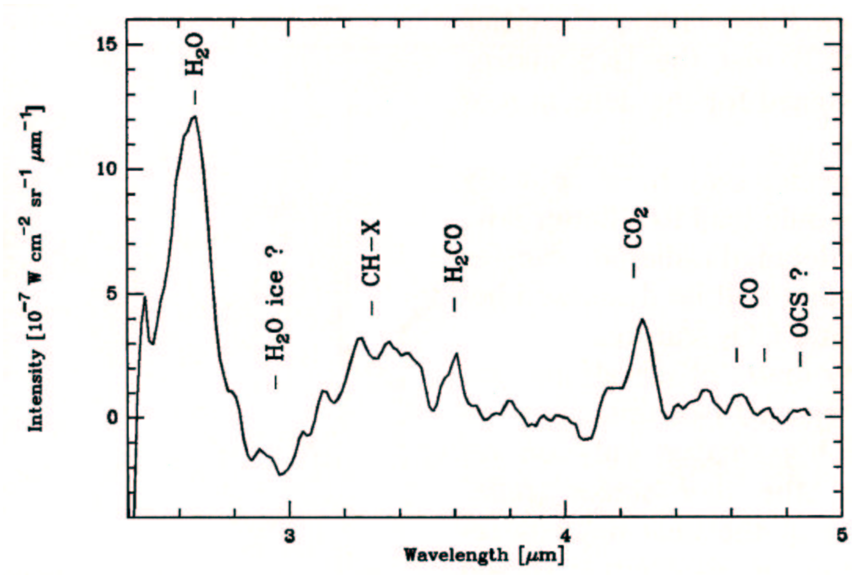


Fig. 3. Infrared spectrum of comet 1P/Halley obtained with the IKS instrument onboard the Vega 1 spacecraft (Combes et al. 1986).

observed at Nançay (Crovisier et al. 2002) or with other radio telescopes. Observations in the centimetric window led to the detection of NH_3, from its 24-GHz inversion lines (tentatively in comet IRAS-Aracki-Alcock and unambiguously in comets Hyakutake and Hale-Bopp), and to the detection of the H_2O 22-GHz line.

The millimetre and submillimetre windows are more favourable than the centimetric window for detecting cometary parent molecules due to larger spontaneous emission rates and smaller beam dilution. These windows produced many discoveries of parent molecules (Table 2). The first species unambiguously detected was HCN at 89 GHz in comet Halley with the 30-m telescope of Institut de Radioastronomie Millimétrique (IRAM) (Fig. 5). CH_3OH and H_2S were discovered in 1990 in comets C/1989 X1 (Austin) and C/1990 K1 (Levy) at IRAM. H_2CO, identified in situ from its protonated ion in mass-spectra obtained onboard Giotto, was also detected in these

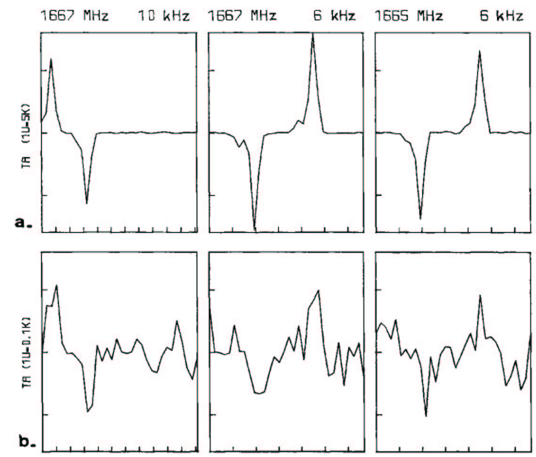


Fig. 4. Observation of OH 1665 and 1667 MHz transitions in comet C/1973 E1 (Kohoutek) with the Nançay radio telescope: a) the galatic source W12 taken as a calibrator; b) the comet in December 1973. Shown are unfolded frequency-switched spectra (from Biraud et al. 1974)

comets. Twelve new identifications (not including isotopes and ions) were made in 1996–1997 in the bright comets Hyakutake and Hale-Bopp, essentially with the Caltech Submillimeter Observatory and the IRAM Plateau de Bure and 30-m telescopes (Table 2). The most complex detected species is ethylene glycol (Fig. 6), which was identified in Hale-Bopp spectra in 2003 when the frequencies of its rotational transitions were published. Last but not least, H_2O was detected in several comets through its fundamental 557 GHz rotational transition, first with the Submillimeter Wave Astronomy Satellite (SWAS) in 1999 in C/1999 H1 (LEE), and with the Odin telescope (Biver et al., this book). Very recently, the NH_3 572-GHz fundamental line was detected with Odin in several comets (Biver et al., this book).

Observations in the millimetre and submillimetre windows provided also key measurements of the D/H ratio in H_2O and HCN, and $^{16}O/^{18}O$, $^{12}C/^{13}C$, $^{14}N/^{15}N$, $^{32}S/^{34}S$ isotopic ratios in H_2O, HCN, CS and H_2S, respectively (see review of Bockelée-Morvan et al. 2004). Molecular ions (CO^+, HCO^+, H_3O^+) were also detected.

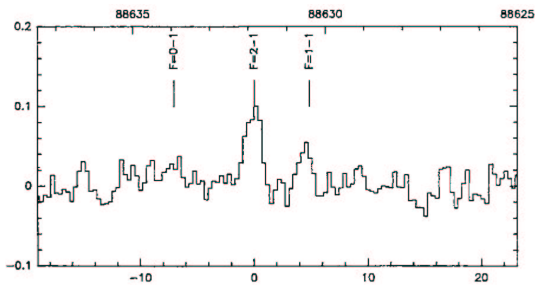


Fig. 5. Historical detection of HCN J(1-0) in comet Halley with the IRAM 30-m telescope in November 1985. The abcissa is the Doppler velocity in the nucleus rest frame in km s^{-1} (Despois et al. 1986).

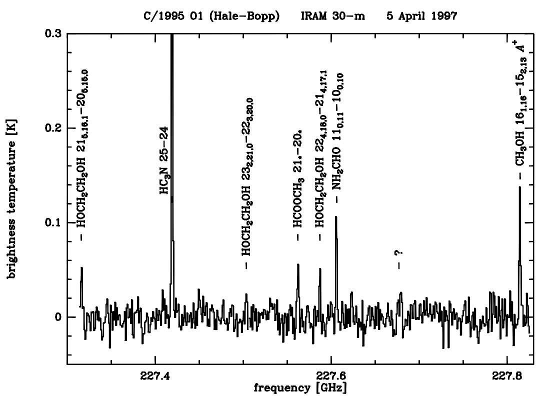


Fig. 6. Detection of ethylene glycol ($HOCH_2CH_2OH$) and other species in comet Hale-Bopp (Crovisier et al. 2004).

3 Conclusion

After 140 years of spectroscopic investigations of cometary atmospheres, our knowledge of comet composition has been greatly improved with about two dozens of parent molecules now identified. Their abundances relative to water are summarized in Fig. 7. Striking similarities with the composi-

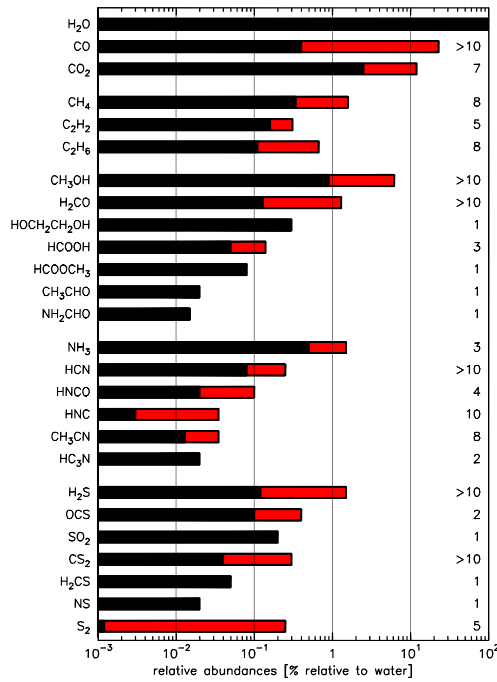
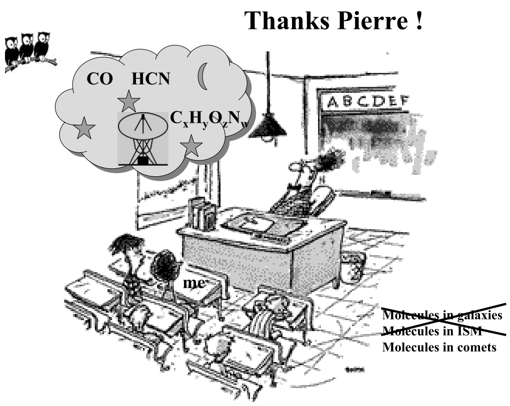


Fig. 7. Abundances relative to water of cometary parent molecules. On the right is given the number of comets in which each molecule has been detected. (adapted from Bockelée-Morvan et al. 2004, courtesy J. Crovisier).

tion of star forming regions are observed suggesting that cometary molecules formed by similar processes. Chemical diversity is observed between comets, which origin is not yet elucidated and may be related to formation in different regions of the solar nebula.

Comet spectroscopic studies will strongly benefit from the instruments of the next generation such as the Herschel Space Observatory and Atacama Large Millimeter Array (ALMA). A wealth of new information is expected from the Rosetta mission at the horizon 2014.



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