

Review

Organic Matter in Cometary Environments

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Abstract: Comets contain primitive material leftover from the formation of the Solar System, making studies of their composition important for understanding the formation of volatile material in the early Solar System. This includes organic molecules, which, for the purpose of this review, we define as compounds with C–H and/or C–C bonds. In this review, we discuss the history and recent breakthroughs of the study of organic matter in comets, from simple organic molecules and photodissociation fragments to large macromolecular structures. We summarize results both from Earth-based studies as well as spacecraft missions to comets, highlighted by the Rosetta mission, which orbited comet 67P/Churyumov–Gerasimenko for two years, providing unprecedented insights into the nature of comets. We conclude with future prospects for the study of organic matter in comets.

Keywords: comet; organics; volatiles; astrobiology



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1. Introduction

Comets are primitive leftovers from the formation of the Solar System. As such, their composition provides clues to physics and chemistry operating during the protoplanetary disk phase (Figure 1), as well as the preceding phases of star formation (e.g., [1,2]). Cometary nuclei consist of a combination of volatile ices and refractory carbonaceous material and silicates [3]. The exact partition (whether comets are “dirty iceballs” or “icy dirtballs”) is still under debate, though results from the recent European Space Agency (ESA) mission Rosetta and other arguments favor an ice-to-dust mass ratio greater than unity (i.e., “icy dirtballs”) [4].

The volatile composition of comets is usually dominated by water (H₂O), with carbon dioxide (CO₂) and carbon monoxide (CO) also being abundant at the 1–20% level compared to H₂O [5,6]. One of the surprising results from the Rosetta mission was the discovery that molecular oxygen (O₂) was very abundant in 67P/Churyumov–Gerasimenko (hereafter 67P), with O₂/H₂O = 110% [7]. However, comets are also rich in simple organic species, such as methanol (CH₃OH), ethane (C₂H₆), methane (CH₄), and hydrogen cyanide (HCN). These species have been detected in comets since the 1990s using observations at infrared (IR) and sub-mm wavelengths [5,8]. Simpler radical species such as diatomic carbon (C₂) and cyanide (CN) have been detected in comets at optical wavelengths since the 19th century. These species are likely released from the photodissociation of molecules such as acetylene (C₂H₂) and HCN, though the origin of many of these species is still not completely understood [6,9]. More recently, much more complex organic molecules such as ethanol (C₂H₅OH), formamide (NH₂CHO), glycolaldehyde (CH₂OHCHO), and acetaldehyde (CH₃CHO) have been detected at sub-mm wavelengths (e.g., [10]). Even glycine, the simplest amino acid, and phosphorous (P, predominantly traced back to PO [11]) were detected by the Rosetta mission [12].

The carbonaceous refractory phase of cometary material also potentially contains organic material, though this phase of cometary material is less understood than the volatile phase. There is observational evidence for polycyclic aromatic hydrocarbons (PAHs) present in cometary material (e.g., [13–19]). In the past, the presence of PAHs in comets has been highly debated, though the detection of toluene at 67P by Rosetta [20] has provided a firm basis for PAHs being present in comets. The Giotto mission flyby of comet 1P/Halley detected the presence of so-called CHON particles (so named because they were rich in carbon, hydrogen, oxygen, and nitrogen) [21]. These CHON particles have been proposed as a possible source for carbon-bearing radicals like C_2 observed at optical wavelengths discussed above (e.g., [22,23]), as well as more complex molecules such as formaldehyde (H_2CO) [24].

As the chemical inventory of species detected in comets is rich in organic molecules, comets are of immense interest as possible sources of Earth's organic material. For the purposes of this review, we adopt the strict chemical definition of organic matter, which encompasses molecules that contain C–H and/or C–C bonds, and focus on species that fit this definition. However, it should be noted that comets are also rich in non-organic species, such as carbon monoxide (CO), carbon dioxide (CO_2) and ammonia (NH_3), that, despite not being strictly organic, are still important in the formation of prebiotic molecules. In this review, we discuss the history of the study of organic matter in comets, recent advances in our understanding of cometary organic matter, and future prospects for the continued study of organic molecules in cometary nuclei.

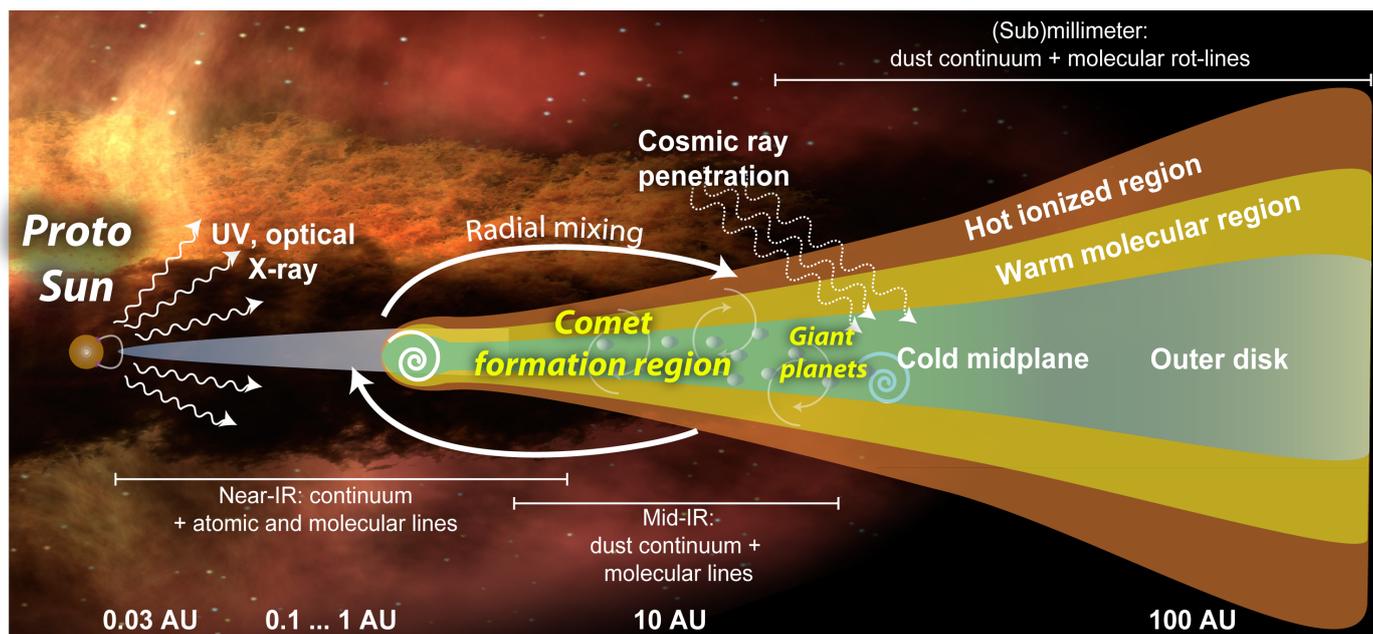


Figure 1. Depiction of a protoplanetary disk and the relevant physical processes. As remote observations of other protoplanetary disks often cannot penetrate deep into the disk, comets serve as our best probes for the physics and chemistry occurring in the cold midplane. Image Credit: Geronimo Villanueva, priv. communication.

2. Tools for Studying Cometary Organic Matter

Studies of cometary composition are often limited to remote sensing of the gas-phase coma (transient gravitationally unbound atmosphere) that surrounds the nucleus of the comet, owing to sublimation of the primary ices H_2O , CO_2 , and CO. These methods employ spectroscopy at a variety of wavelengths to observe electronic, vibrational, rotational, and rovibrational transitions of molecules of interest in the gas phase. More recently, spacecraft missions have enabled studies of the solid phase of cometary material, most notably through sample return of refractory material (dust) by the Stardust mission and the lander Philae (associated with the Rosetta mission), which was able to perform in situ

analysis on the comet's surface. In situ missions also sample the coma gas through mass spectroscopy. We discuss these methods below.

2.1. Remote Sensing

2.1.1. Optical

Optical observations of comets (which we define as covering wavelengths from 300–1000 nm) have the longest history, with the first spectra of comets being obtained in the 19th century [25–27]. Comets show a rich emission line spectrum at optical wavelengths, dominated by emissions from CN and C₂ (see Figure 2). Many of these molecules are carbon-bearing and are likely fragments of more complex organic matter present in cometary ices and dust. Narrowband filter sets have also been developed so that imaging techniques can be used to isolate molecules of interest [28].

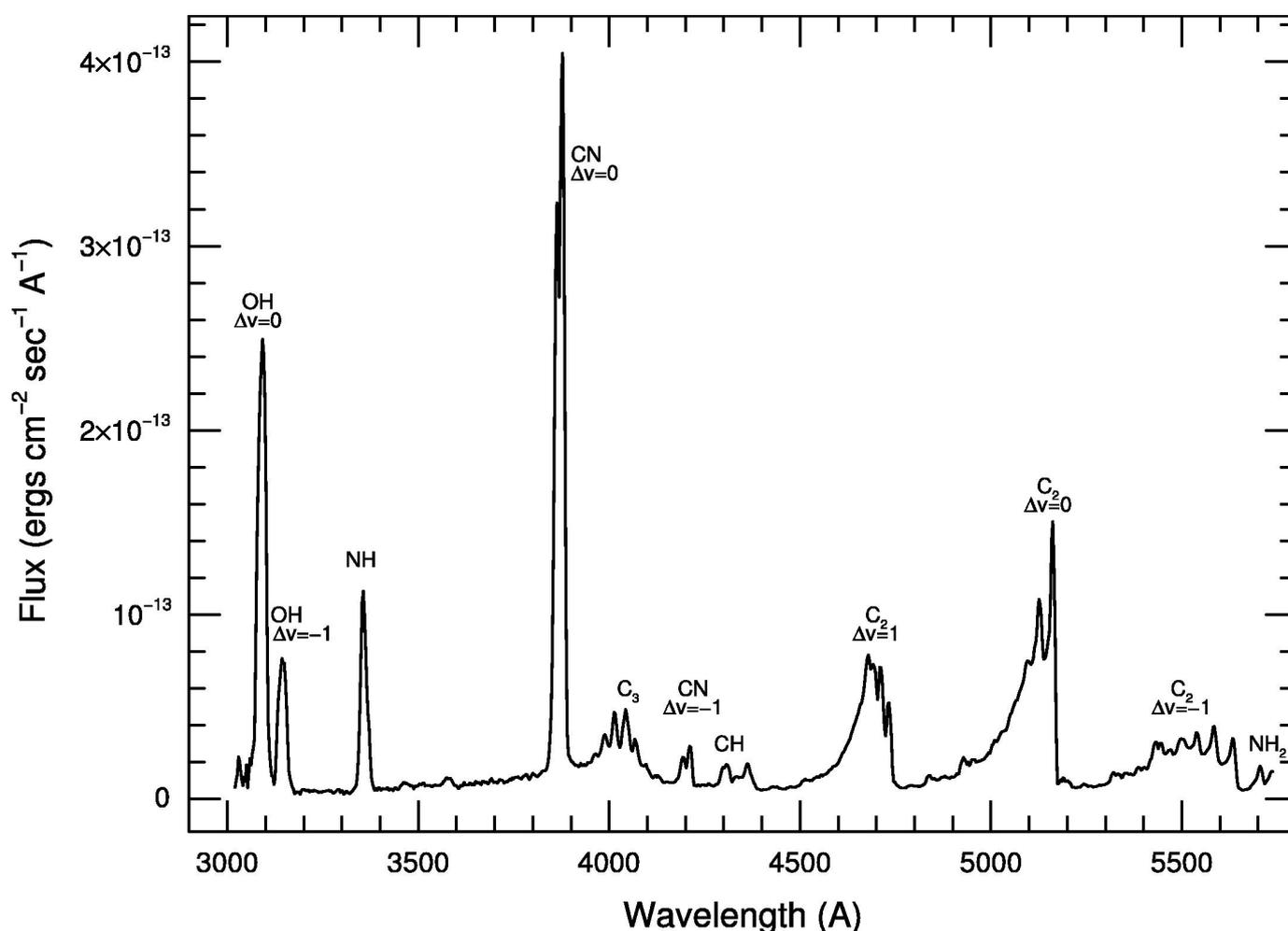


Figure 2. Optical spectrum of comet 122P/De Vico showing typical emissions observed in cometary spectra. Many of these species are likely released via the photodestruction of simple organic matter or carbon-rich dust grains. Figure from [29].

Over 200 comets have been characterized at optical wavelengths (e.g., [29–32]). These studies have revealed several taxonomic groups, including comets that are depleted in carbon-chain species, and provided the first glimpse into variations in composition among comets (see Section 3.9.2). However, due to the fragment nature of the observed species and our lack of understanding of the coma processes responsible for their release [9,33], interpretation of these taxonomic groupings in terms of the more complex organic matter that they likely trace is difficult.

Optical spectroscopy at high spectral resolution has also proven to be a powerful method for determining isotopic ratios for C and N in cometary material. The first isotopic

measurements in C and N came from the CN molecule [34,35], with some carbon measurements also coming from observations of C₂ [36]. More recently, NH₂ has been utilized to measure isotopic ratios in N [37–39]. These measurements revealed Earth-like ratios in C, but ratios in N deviate from the terrestrial value by a factor of two and solar value by a factor of three. The reason for this discrepancy is not fully understood (see Section 3.9.1).

2.1.2. Near Infrared (NIR)

NIR observations of comets were pioneered in the 1980s, resulting in the first direct detection of H₂O from a comet [40]. The development of ground-based high spectral resolution instruments in the 1990s resulted in the first observations of a wider volatile composition of comets at IR wavelengths (e.g., [41,42]), with individual organic molecules such as CH₄, C₂H₆, and acetylene (C₂H₂) identified for the first time (see Figure 3). NIR observations at high spectral resolution are the only way to directly study symmetric hydrocarbons such as C₂H₆, C₂H₂, and CH₄ in comets with remote facilities, as these species lack a permanent dipole moment and pure rotational transitions, precluding their measure at millimeter/sub-millimeter wavelengths (see Section 2.1.3). Low spectral resolution IR observations are also diagnostic of organic matter, but to date have mostly been applied to observations of cometary surfaces visited by spacecrafts (see Section 2.2).

2.1.3. Mm/Sub-mm

Observations at millimeter (mm) and submillimeter (sub-mm) wavelengths have a similar history to the NIR, with observations dating as far back as the 1970s (e.g., [43,44]). Advances in instrumentation in the 1990s first enabled the regular detection of a suite of molecules in comets at mm/sub-mm wavelengths. These observations have the advantage of being sensitive to more complex species than are observed at optical/NIR wavelengths, such as formamide and ethanol, through their rotational transitions. Sub-mm observations also have higher spectral resolution than optical/IR observations, enabling velocity-resolved studies of coma species via the analysis of their spectral line profiles. These observations measure molecular outflow velocities, and can reveal potential coma outgassing asymmetries. However, this often comes at the expense of spatial resolution on the sky. Early cometary observations were dominated by single-dish telescopes (e.g., [45–47]) with an angular resolution on the scale of several to tens of arcseconds (corresponding to thousands of kilometers projected distance at the comet). The development of interferometers, including, but not limited to, the Atacama Large Millimeter/Submillimeter array (ALMA), with sub-arcsecond spatial resolution has revolutionized the study of organic molecules in comets, providing spatially resolved maps of the distributions of species such as HCN, H₂CO, and CH₃OH (see Figure 4) (e.g., [48–50]).

2.2. Spacecraft Missions

Spacecraft missions to comets have proven invaluable to the study of comets in general and specifically organic matter in comets, providing observations of the nucleus and compositional information only attainable in situ. Below we highlight a few missions with a particularly large impact on our knowledge of organic matter in comets.

2.2.1. The Halley Armada

The first comet to be studied via spacecraft flybys of the nucleus was 1P/Halley in 1986. A suite of spacecrafts flew by the comet, including ESA's Giotto mission and the Soviet probe Vega 2. Giotto carried a mass spectrometer that measured the composition of the coma in situ for the first time [51]. It also obtained IR spectra showing the presence of H₂O, CO, CO₂, and organic matter [13]. Vega 2 provided optical and IR spectra of the inner coma, providing the first evidence for the presence of PAHs in comets (e.g., [18]).

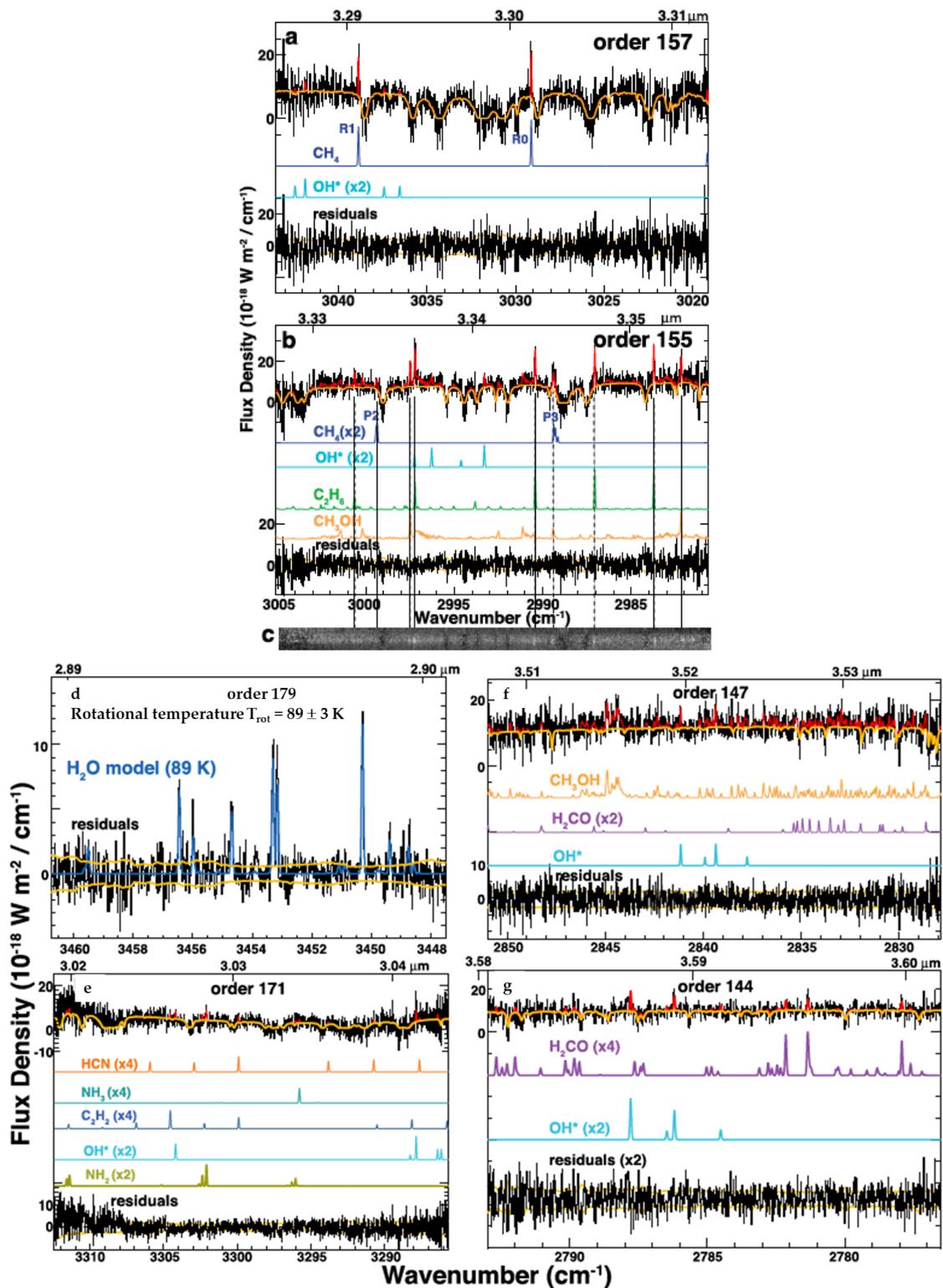


Figure 3. IR spectra of comet 45P/Honda-Mrkos-Pajdušáková obtained with iSHELL on the NASA Infrared Telescope Facility (IRTF) showing spectral regions containing typical emissions observed in cometary spectra. These include CH_4 (a and b), C_2H_6 (b), CH_3OH (b and c), H_2O (d), H_2CO (f and g), HCN , C_2H_2 , and NH_3 (e). In particular, high spectral resolution IR spectroscopy is the only method to remotely observe symmetric hydrocarbons like C_2H_6 and CH_4 in comets due to their lack of pure rotational transitions. The observed spectra are in black, with fluorescence models overplotted in red and fits for individual species offset below the observed spectrum. The “*” after OH in the model labels indicates these emissions are prompt emission, while all other emissions are fluorescence. Figure from [52].

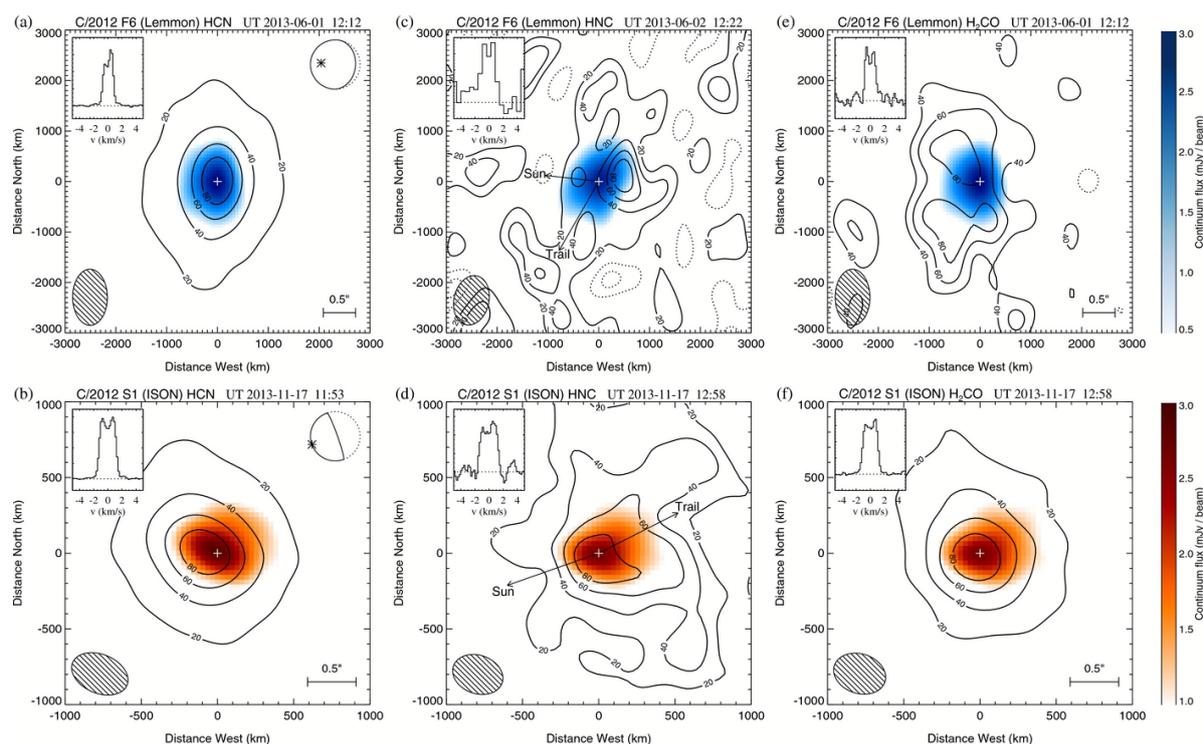


Figure 4. ALMA maps of the spatial distribution of HCN (a,b), HNC (c,d), and H₂CO (e,f) in two comets: C/2012 F6 (Lemmon) (a,c,e) and C/2012 S1 (ISON) (b,d,f). The contours represent the line emission of the respective gas species, while the color scale shows the continuum emission from the dust coma. Figure from [48].

2.2.2. Stardust

NASA's Stardust mission is to date the only mission to return cometary material for analysis in Earth-based laboratories [53]. The spacecraft performed a flyby of comet 81P/Wild 2 on 2 January 2004, collecting dust particles from the coma in aerogel. These samples were then successfully returned to Earth two years later on 15 January 2006. With the ability to analyze the collected dust particles in state-of-the-art Earth-based laboratories rather than the necessarily limited instruments on a spacecraft, a wealth of studies have been performed, ranging from isotopic composition to the presence of organic material (e.g., [16,53,54]), including the amino acid glycine [55]. Related to these particles is the study of interplanetary dust particles (IDPs), which are collected from the upper layers of the Earth's atmosphere (e.g., [56,57]). These particles may very well have a cometary origin, but determining a definitive link to a specific comet is difficult, though it has been attempted (e.g., [58]).

2.2.3. Rosetta

The Rosetta mission provided huge leaps forward in our understanding of comets and their molecular composition (see Figure 5). Impactful instruments of the many on board include the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) mass spectrometer and the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) IR spectrometer, as well as the Cometary Sampling and Composition (COSAC) and Ptolemy mass spectrometers on the Philae lander. ROSINA was able to perform an in situ analysis of the coma gas around the target comet, 67P/Churyumov-Gerasimenko. These observations provided extensive measurements of species previously known in comets, but also discovered many new species never before detected in comets. These include complex organic molecules that are beyond the grasp of current Earth-based observation techniques, such as glycine [12], due to their low abundance and complex spectra. COSAC and Ptolemy on the Philae lander were able to perform a similar in situ analysis of the surface material. Although the Philae lander only operated for a few days due to power constraints created

by a non-optimal landing configuration, COSAC and Ptolemy still provided the first measurements directly from the surface of a cometary nucleus (see [59] for a complete review of Philae results). The VIRTIS instrument provided NIR spectroscopy of the surface of 67P revealing the presence of water and CO₂ ice [60–62], as well as an organic absorption feature around 3.2 microns ([63,64], see Figure 6).

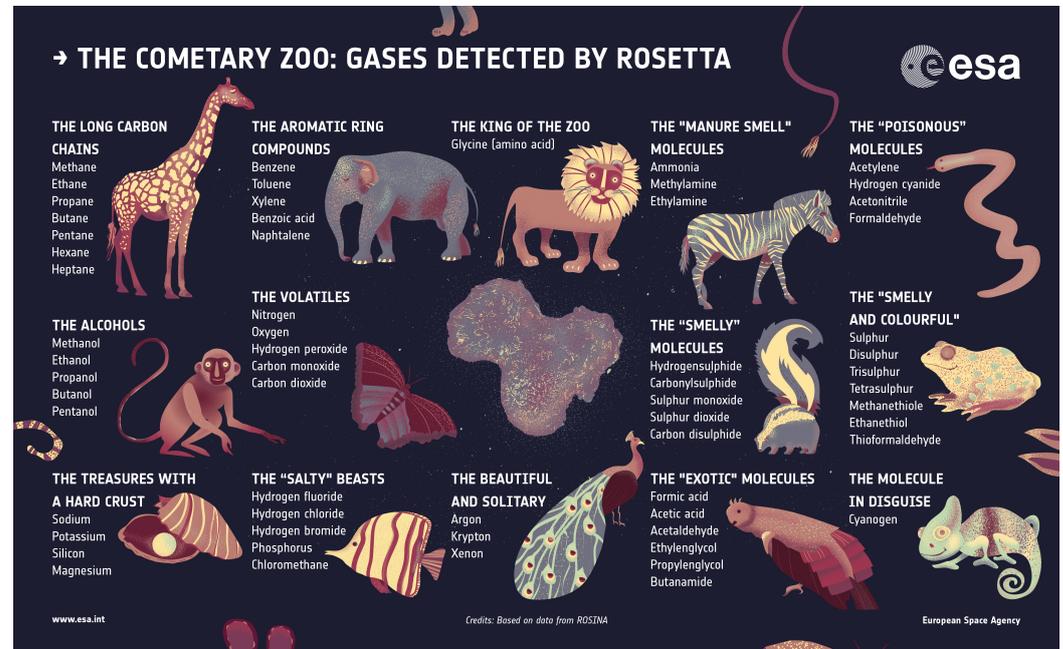


Figure 5. A graphic representation of all gases detected by the Rosetta mission, depicted here as the "Cometary Zoo". Many of these species are organic molecules and were detected for the first time in a cometary coma by Rosetta. Image Credit: ESA.

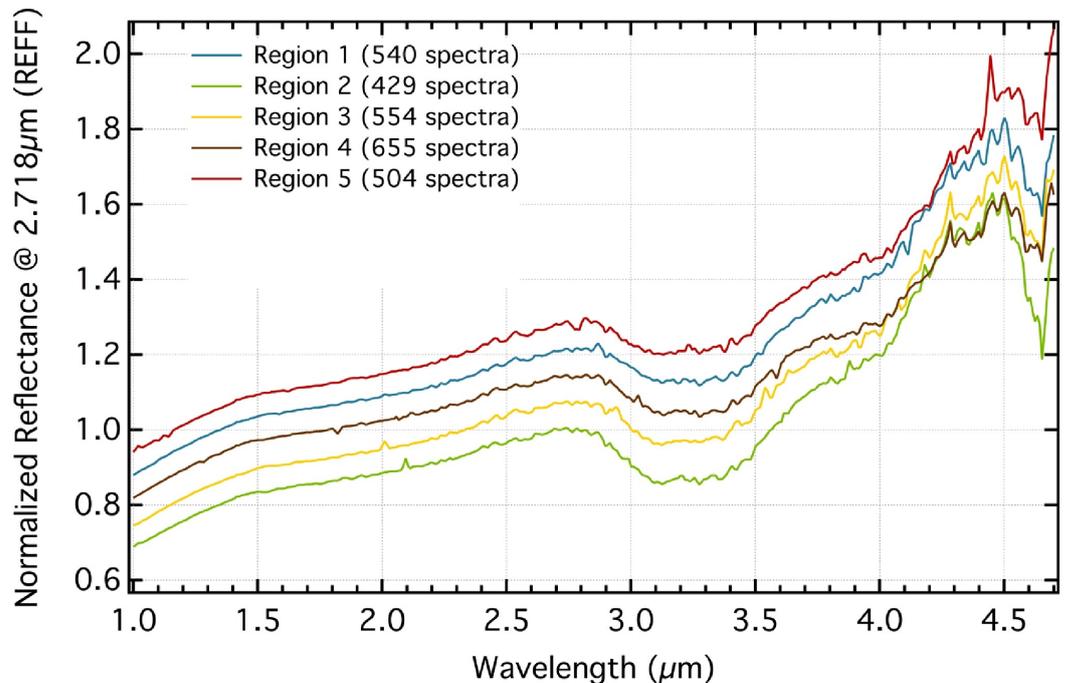


Figure 6. Spectra of several regions on the surface of 67P showing strong absorption at 3.0–3.5 μ m, which is attributable in part to the presence of organic matter. Figure from [63].

3. Results for Specific Species

Table 1 lists the organic molecules detected via the Earth-based remote sensing of cometary comae with information pertaining to the number of comets in which this species has been detected and typical abundances. For a list of additional organic species detected by Rosetta and Philae, see Table 4 of Altwegg et al. 2019 [65]. Below, we summarize recent results pertaining to specific species or types of organic matter detected in comets. This includes parent (or primary) species that are inherently present in the nucleus, as well as daughter (or secondary) species that are produced by photolysis in the coma. More details regarding the volatile composition of comets can be found in recent reviews/survey studies (e.g., [5,6,8,65–68]).

Table 1. Organic molecules detected in comets via Earth-based remote sensing. Does not include species only detected by Rosetta at 67P, though Rosetta measurements are included in the statistics. Based on compilation of Dello Russo et al. 2016 [8] and Bockelee-Morvan and Biver 2017 [67], updated with more recent observations as of July 2020. See Table A1 for the list of comets with recent observations.

Species	Chemical Formula	Typical Abundance (X/H ₂ O in %)	Number of Comets
Hydrogen Cyanide	HCN	0.1–0.2 ^a	57
Hydrogen Isocyanide	HNC	0.01	21
Isocyanic Acid	HNCO	0.02	16
Acetonitrile	CH ₃ CN	0.02	22
Cyanoacetylene	HC ₃ N	0.02	11
Acetylene	C ₂ H ₂	0.13	30
Methane	CH ₄	0.72	32
Ethane	C ₂ H ₆	0.52	35
Formaldehyde	H ₂ CO	0.30	31
Methanol	CH ₃ OH	2.05	35
Formic Acid	HCOOH	0.09	10
Methyl Formate	HCOOCH ₃	0.003–0.08	3
Acetaldehyde	CH ₃ CHO	0.05–0.08	4
Ethylene Glycol	(CH ₂ OH) ₂	0.01–0.35	5
Ethanol	C ₂ H ₅ OH	0.04–0.12	2
Glycolaldehyde	CH ₂ OHCHO	0.02	2
Formamide	NH ₂ CHO	0.004–0.021	5
Thioformaldehyde	H ₂ CS	0.003–0.09	4

^a The mean value for sub-mm observations is 0.1%, while the mean value for IR observations is 0.2%. See Section 3.1.

3.1. HCN and HNC

Hydrogen cyanide (HCN) is a key precursor in the synthesis of amino acids and is likely integral to the presence of life on Earth [69]. It was first securely detected in comet 1P/Halley [70,71] and is routinely sampled in comets with state-of-the-art instruments, through its intrinsically strong pure rotational and ro-vibrational transitions in the mm/sub-mm and in the near-infrared, respectively. HCN is one of the main reservoirs of volatile nitrogen in comets (as opposed to the total nitrogen, which may be locked up in more refractory material such as ammonium salts [72,73]) and a likely parent of the fragment species CN (see Section 3.9.1) [23,74,75]. Long-slit near-IR observations (e.g., [8]) and spatially resolved interferometric studies [48] have indicated that the distribution of HCN is consistent with direct sublimation from the nucleus, (i.e., a parent species, see Figure 4). Interestingly, HCN abundances as measured in the near-IR for a given comet can be two to three times higher than those measured at mm/sub-mm wavelengths [67], even when comparing to ALMA measurements with a beam size comparable to that of near-IR instruments. The reason for this discrepancy is not understood. Depending on the wavelength of the study, average HCN abundances compared to H₂O in comets range from 0.1–0.2% [67,75].

Hydrogen isocyanide (HNC), an isomer of HCN, was first detected in comet C/1996

B2 (Hyakutake) [76], with an HNC/HCN abundance ratio in agreement with interstellar values. However, the strong heliocentric dependence of the HNC/HCN ratio in C/1995 O1 (Hale–Bopp) [77] indicated that cometary HNC is more consistent with production from coma sources. Various formation mechanisms, from the isomerization of HCN to thermal degradation of polymers [78,79] have been proposed. A review of 11 comets confirmed a strong heliocentric dependence in the HNC/HCN ratio that was incompatible with direct release from the nucleus [80]. More recent work with ALMA in comet C/2012 S1 (ISON) revealed HNC production following the release of a clump of ice- or organic-rich material from the nucleus [49]. Owing to the absence of the clump in simultaneously observed images of H₂CO or CH₃OH, it was concluded that the clump was more likely rich in polymeric or macromolecular organic matter, making the HNC parent more consistent with a refractory component (see Section 3.8) than an ice one.

3.2. H₂CO

Formaldehyde (H₂CO) is a chemical precursor to sugars, and similar to HCN, can be measured with both mm/sub-mm and NIR studies. It was first unambiguously detected at mm wavelengths in comets C/1990 V (Austin) and C/1990 XX (Levy) [81,82], although tentative detections were claimed during flyby and ground-based observations of 1P/Halley [13,83–85]. Measurements of H₂CO⁺ by the neutral mass spectrometer on board the Giotto spacecraft provided the first indication of H₂CO production by an unknown parent in the coma [86]. More recent studies of H₂CO at mm wavelengths in comets indicated production from unknown parent source(s) with a scale length of 7000 km at 1 AU [24,45,87], and sub-mm ALMA observations of the inner coma indicate a parent scale length of 1000–5000 km [48,49]. On the other hand, NIR observations, which are most sensitive to the near-nucleus region, have indicated that H₂CO can also be released directly from the nucleus [75,88], suggesting that both nucleus and coma sources can contribute to H₂CO production in comets. Regardless of the nature of its release, H₂CO has abundances ranging from 0.04–1.3% with respect to H₂O in comets measured to date [67,75].

Collectively, these results have shown that H₂CO is one of a number of molecules which is inconsistent with direct release from the nucleus alone and is likely produced by unidentified coma sources (“distributed” sources; [89]). The visible, infrared and thermal imaging spectrometer (VIRTIS) instrument onboard Rosetta detected organic macromolecular material that is likely the source for some of these unidentified parents [90]. Degradation of the H₂CO polymer, polyoxymethylene (POM), was proposed to explain the heliocentric dependence of H₂CO production in comet C/1995 O1 (Hale–Bopp) [91] and may be the unidentified H₂CO parent, though this has yet to be confirmed (see Section 3.8). Analysis of the data obtained by the ROSINA instrument onboard Rosetta concluded that the presence of POM is unlikely [20]. Further studies of cometary H₂CO, particularly spatially resolved interferometry with facilities such as ALMA combined with new spacecraft missions (particularly volatile sample return), will be necessary to help identify its parent source.

3.3. CH₃OH

Methanol (CH₃OH) is the simplest alcohol and is the starting point for the formation of more complex organic molecules in the interstellar medium (ISM) [92–94]. It was first detected in comets at mm wavelengths [95], and has since been measured in many comets at mm/sub-mm and near-infrared wavelengths [67,75]. The heliocentric dependence of CH₃OH production, combined with long-slit near-infrared studies and spatially resolved ALMA observations, has shown that it is primarily associated with direct nucleus release [46,50,75]. However, ground-based measurements of hyperactive comet 103P/Hartley 2 indicated increased anti-sunward CH₃OH and H₂O production that was associated with sublimation from icy coma grains [96–99]. This phenomenon was also observed in comet C/2007 W1 (Boattini) (see Figure 7, panel a) [100]. CH₃OH is one of the more abundant species in comets, ranging from 0.4–6.2% relative to H₂O [67,75].

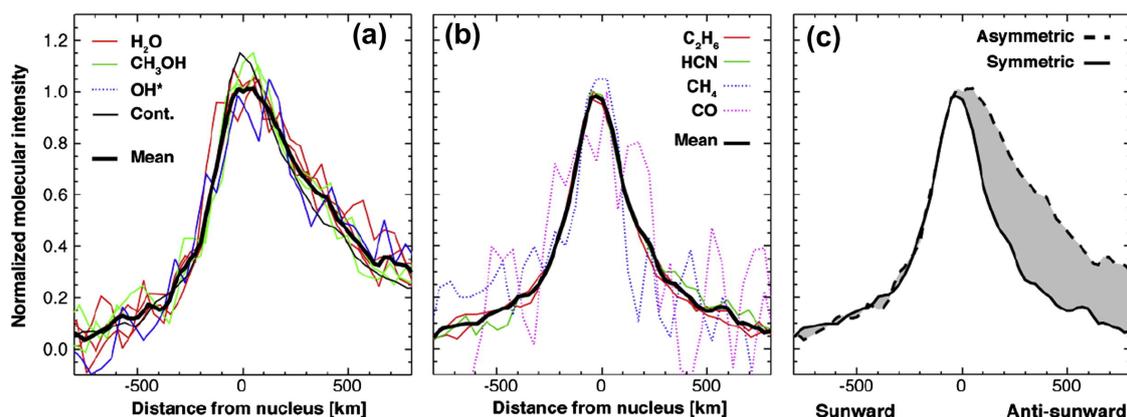


Figure 7. Spatial profiles for various species observed in comet C/2007 W1 (Boattini) at IR wavelengths. Panel (a) shows H₂O, CH₃OH, OH (a tracer for H₂O), and the dust continuum, while panel (b) shows C₂H₆, HCN, CH₄, and CO. The “*” after the OH label indicates the emissions used to measure the spatial distribution are prompt emission, while all other emissions are fluorescence. Panel (c) shows the average profile of the species in each panel, and the grey shading highlights the difference between the two profiles. The species in panel (a) are spatially extended in the antisunward direction (positive x values), while the species in panel (b) are symmetric. This indicates different modes of release for the different volatiles. Figure from [100].

In addition to its likely origin as a parent molecule in comets, CH₃OH has proven invaluable for probing coma temperatures and thermal physics in comets. Multiple CH₃OH lines are routinely used to measure coma rotational and/or kinetic temperatures (e.g., [95]). Coupled with spatially resolved sub-mm observations, detailed CH₃OH maps can show variations in rotational and kinetic temperature with nucleocentric distance, revealing the thermal physics of the inner coma [50].

3.4. C₂H₆

C₂H₆ was first detected in a cometary coma in C/1996 B2 (Hyakutake) [101], and is responsible for one of the brightest emission bands observed in comets at NIR wavelengths. It is also a relatively abundant trace species present in comets, with an average abundance of 0.55% compared to H₂O, though in the sample of comets studied to date, there is a factor of two difference between the average C₂H₆ abundance in Oort cloud comets (OCCs, comets whose dynamical reservoir is the Oort cloud) compared to the average value for Jupiter family comets (JFCs, comets whose orbits are dynamically linked to Jupiter and are thought to have been perturbed inward from the scattered disk) [8]. As a symmetric molecule, C₂H₆ does not have a permanent dipole moment and therefore is not observable at sub-mm wavelengths. C₂H₆ in comets was likely formed from the addition of hydrogen atoms to simpler hydrocarbons such as C₂H₂ via grain-surface reactions [101–103], but C₂H₆ can also be formed from the irradiation of CH₄ ices [101,104,105]. Irradiation of C₂H₆ can in turn result in the formation of more complex hydrocarbons [106].

Because of the intrinsic brightness of C₂H₆ lines, studies of the spatial distribution of C₂H₆ have been utilized to determine how C₂H₆ is released into the coma. For example, spatial profiles in comet C/2007 W1 (Boattini) showed a similarity with HCN, yet were different than those observed for H₂O and CH₃OH, which was interpreted as evidence for these molecules being stored in different ice phases in the nucleus (see Figure 7) [100]. A similar phenomenon was observed for 103P/Hartley 2, prompting the suggestion of an ice phase dominated by polar molecules such as H₂O and CH₃OH and a different ice phase featuring apolar molecules such as CO₂ and C₂H₆ [96,97,99]. Observations of comet C/2013 V5 (Oukaimeden) with Keck NIRSPEC showed a time variable C₂H₆/H₂O ratio on the order of days, further illustrating that C₂H₆ and H₂O ices are not co-located in the nucleus [107].

3.5. CH₄

Like C₂H₆, CH₄ is a symmetric hydrocarbon and therefore is only observable through its IR rovibrational transitions. However, the CH₄ lines observable are intrinsically weaker than C₂H₆ emissions, making CH₄ harder to detect in cometary comae. Moreover, strong CH₄ absorptions from the Earth's atmosphere (telluric absorptions) make it only possible to observe CH₄ from the ground for certain observing geometries, requiring a sufficient geocentric velocity to Doppler-shift cometary CH₄ emissions away from the corresponding telluric absorptions (see Figure 8). The requirement to achieve this geometry makes observations of CH₄ even more limited in comets, especially for JFCs, which are generally fainter and have lower production rates than OCCs and thus must be observed near closest approach to Earth. This necessarily coincides with a low geocentric velocity, precluding the measurement of CH₄ and resulting in relatively few measurements of CH₄ in JFCs and thus a significant gap in our understanding of its abundance in this dynamical class. Space-based observations do not suffer from this limitation, though to date, space-based platforms have generally not been able to observe CH₄ in comets, and the vast majority of observations of cometary CH₄ have come from ground-based facilities [8]. An exception is the Rosetta mission, where CH₄ was detected using IR observations with the VIRTIS instrument [108] and mass spectrometry with ROSINA [109].

The average CH₄ abundance in comets with respect to H₂O is 0.78%; though similar to C₂H₆, there is a strong difference in the mean values between OCC's (0.88%) and JFC's (0.31%) [8]. However, as noted above, the statistics for CH₄ in JFCs are far from robust. Recent years have provided several rare and favorable opportunities to observe CH₄ in JFCs [52,110–114], providing a much needed boost towards establishing a statistically significant sample of CH₄ measurements in JFCs. However, it is still much smaller than the OCC sample, making comparisons between the two classes more difficult. Therefore, further studies of CH₄ in JFCs are required for definitive comparisons between these two major dynamical families. CH₄ is likely formed from hydrogen addition reactions on atomic carbon on dust grain surfaces [115], and, as mentioned above, the irradiation of CH₄ ices can lead to the formation of C₂H₆ and more complex hydrocarbons.

3.6. C₂H₂

C₂H₂ is another symmetric hydrocarbon observed in cometary comae that has only been detected remotely at IR wavelengths, though it has been detected by ROSINA via mass spectrometry [109]. While its emissions do not suffer from corresponding telluric extinction like CH₄ does, lines of cometary C₂H₂ are generally weak, and it also has a lower mean abundance than either C₂H₆ or CH₄ (average C₂H₂/H₂O = 0.13%, see Table 1), making it more challenging to detect. Similar to C₂H₆ and CH₄, there seems to be a factor of two difference in average C₂H₂ abundances between JFCs and OCCs, with JFCs having lower abundances. C₂H₂ can be formed in the ISM through reactions between atomic carbon and molecular hydrogen [116], and like C₂H₆, can serve as the starting point for the formation of complex hydrocarbons such as benzene [117,118]. C₂H₂ is the most likely volatile parent molecule for the C₂ radical, but often is not the sole source of C₂ (see Section 3.9.2).

3.7. Other Organic Molecules

In addition to the commonly detected molecules detailed above, other complex organic molecules have been detected in comets. For ground-based observations, this has been limited to the brightest comets, such as C/1995 O1 (Hale–Bopp) and C/2014 Q2 (Lovejoy). These larger molecules are accessed via their rotational transitions at mm/sub-mm wavelengths. These include CHO-bearing molecules such as formic acid (HCOOH), methyl formate (HCOOCH₃), ethylene glycol ((CH₂OH)₂), acetaldehyde (CH₃CHO), ethanol (C₂H₅OH), and the simplest monosaccharide sugar, glycolaldehyde (CH₂OHCHO). It also includes nitrogen-bearing species such as isocyanic acid (HNCO), cyanoacetylene (HC₃N), acetonitrile (CH₃CN), and formamide (NH₂CHO), as well as the sulfur-bearing

organic molecule thioformaldehyde (H_2CS) [10,87,119,120]. Owing to them being measured in so few comets, their abundances across the population are very poorly constrained, yet their detection illustrates the record of complex chemistry stored in cometary nuclei. Furthermore, the in situ results from both the mass spectrometer ROSINA aboard Rosetta, as well as COSAC and Ptolemy on the Philae lander, revealed a suite of complex organic molecules in 67P never before detected in comets. Philae was able to detect a number of complex organic molecules only observed in bright comets remotely, such as acetonitrile and ethylene glycol, as well as organic molecules not previously detected in comets, such as acetone ($(\text{CH}_3)_2\text{CO}$) [121]. Many of these molecules were also detected in the coma by ROSINA [20].

The amino acid glycine was detected in samples returned from 81P by the Stardust mission [55]. Glycine was also detected around 67P by Rosetta [12], and further analysis showed that glycine had a distributed source, consistent with release from dust grains in the coma [122].

3.8. Complex Hydrocarbons, PAHs, and CHON Particles

The first evidence for complex macromolecular organic matter dates back to the Halley flybys, with spacecraft determining the presence of complex organic matter in the coma (often referred to as CHON particles) [21]. The Giotto mission also found evidence for a distributed source of H_2CO (i.e., H_2CO not released directly from the nucleus). This was initially viewed as evidence for the presence of POM [86] (Section 3.2). Results from the Ptolemy instrument on the Philae lander on comet 67P from the Rosetta mission showed evidence for POM [123], however measurements from the spacecraft in the coma from ROSINA could not confirm this finding [20]. Evidence for the presence in the dust grains of large macromolecular organic matter similar to that in meteorites was found by Rosetta [124].

The presence of PAHs in comets has been a subject of some controversy. Optical and IR spectra obtained by the Giotto and Vega 2 flybys showed evidence for emissions that could be assigned to PAHs (e.g., [13,18]). Spitzer observations revealed candidate PAH emissions from comet 9P/Tempel 1 [15] after the Deep Impact experiment, which launched a copper impactor into the surface of the comet in order to excavate material from the subsurface to be studied [125]. More recent ground-based studies have found unidentified emission features in the IR spectra of comet 21P/Giacobini-Zinner, which were interpreted as possible emissions from PAHs [19]. IR spectroscopy of the surface of 67P by VIRTIS on Rosetta revealed spectral signatures consistent with PAHs, though the more readily identified features are aliphatic [64]. The PAH toluene was definitively detected by ROSINA and tentatively detected by Ptolemy on the Philae lander at 67P [20], providing the most firm evidence to date of PAHs in comets.

The Stardust and Rosetta missions provided further evidence for complex refractory organic matter in comets. Particles returned by the Stardust mission contained complex organic matter [16,126]. Evidence for both aliphatic and aromatic hydrocarbons was provided both by mass spectrometry in the coma [127], as well as IR spectroscopy of the surface [64]. These hydrocarbons included species as complex as toluene and heptane (see Figure 9) [127].

3.9. Organic Tracers

While optical observations are not sensitive to parent organic molecules that are observed at IR and sub-mm wavelengths, they provide abundances of simpler radical species (CN , C_2 , CH , and C_3) that are produced via the photochemistry of organic matter (see Figure 2). As the sample size of optical observations is much larger than IR/sub-mm observations (>200 comets in the optical vs. ~50 in the IR/sub-mm), they represent the most extensive database for the organic composition of comets, even if linking their abundances to parent organic molecules is not straightforward. In this section, we describe the current knowledge of these organic tracers and their links to parent organic molecules.

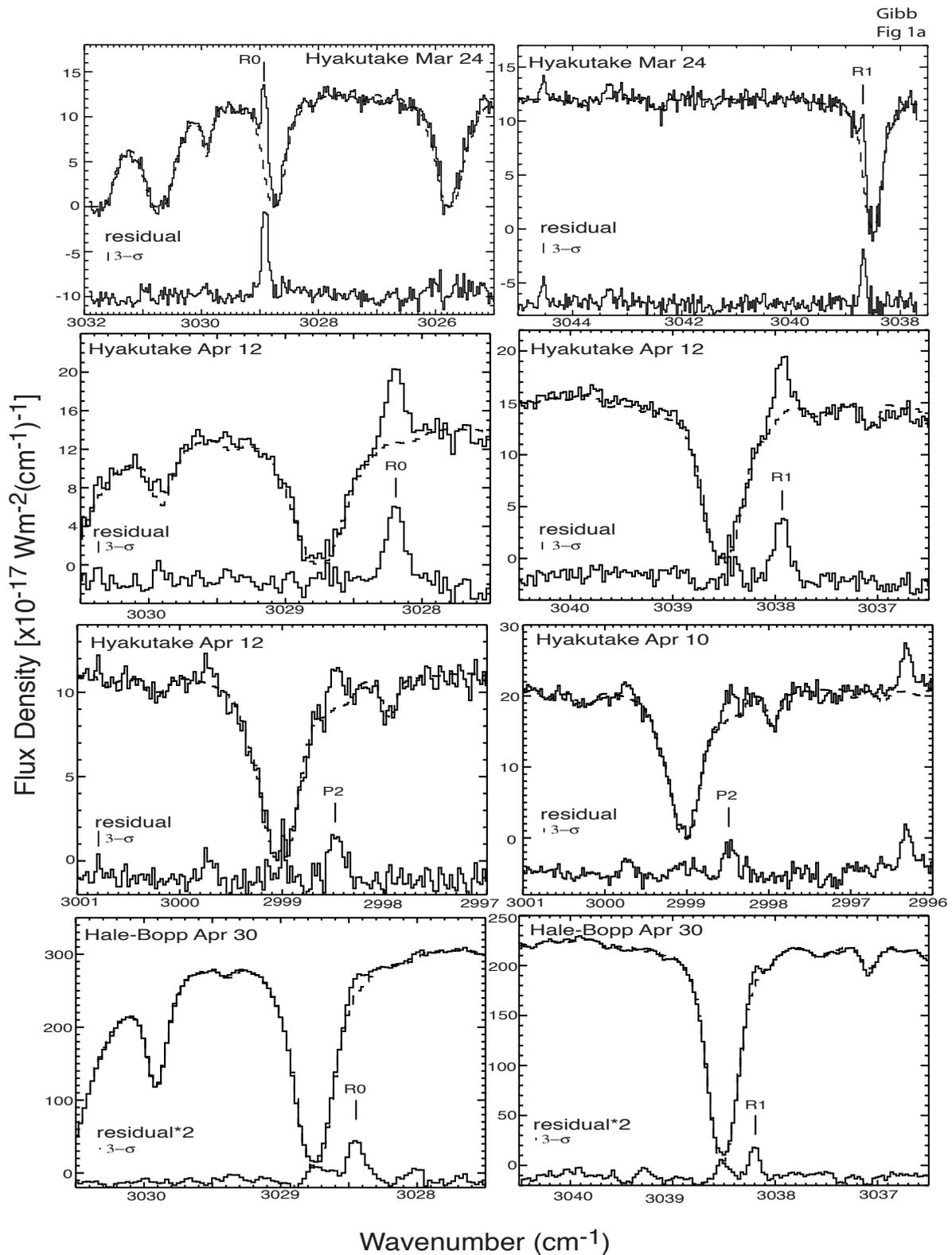


Figure 8. IR spectra showing CH_4 emissions in comets C/1996 B2 (Hyakutake) (top six panels) and C/1995 O1 (Hale–Bopp) (bottom two panels). The measured spectra (complete with continuum) are shown above, whereas the continuum removed spectra are shown below in each panel, labeled as residual. For Hale–Bopp, the continuum removed spectra are multiplied by a factor of two, indicated by “residual*2”. The strong absorptions are due to telluric CH_4 , illustrating the need for cometary emissions to be Doppler-shifted away from the center of these features by sufficient geocentric velocity of the comet. Figure from [128].

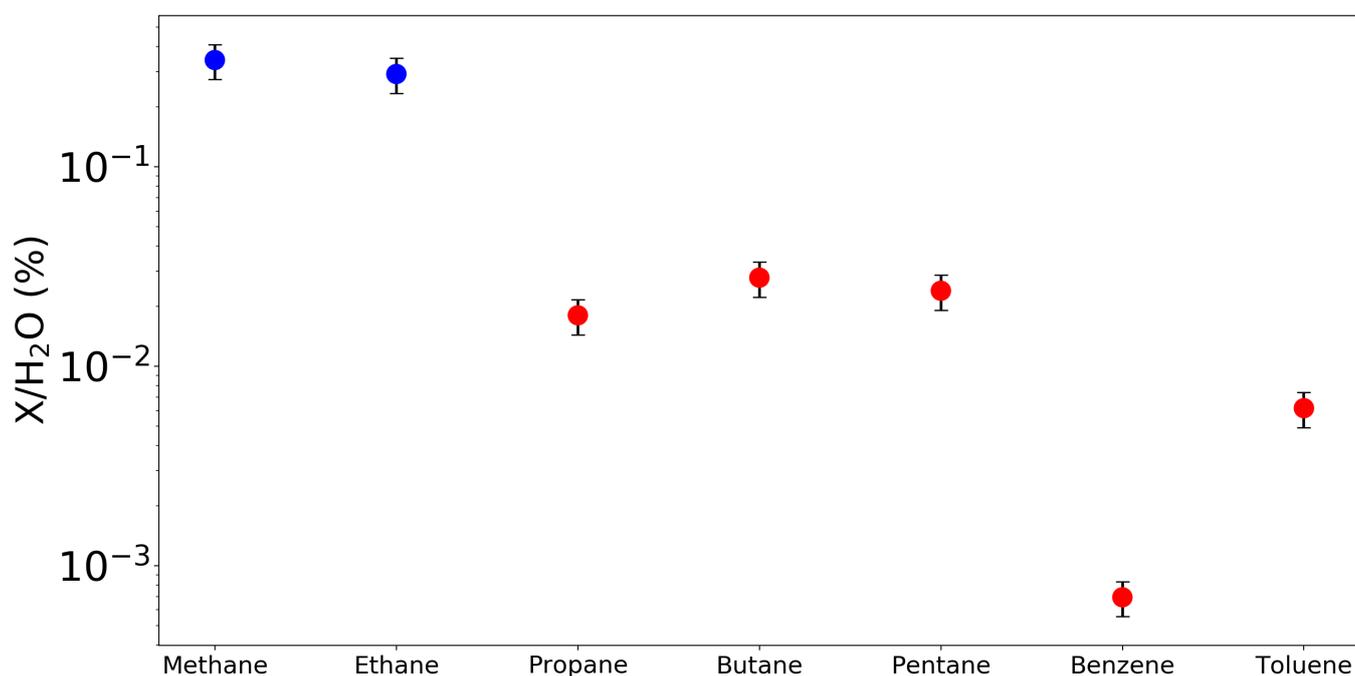


Figure 9. Plot showing the abundances compared to H₂O of various hydrocarbons detected by ROSINA in the coma of 67P at a heliocentric distance of 1.52 AU in May 2015. While butane and pentane were not detected in May 2015, they were detected in May 2016, when all hydrocarbons abundances relative to water were significantly higher than in May 2015. To account for this, the values plotted are their May 2016 measurements scaled by their mixing ratios compared to methane. Blue points represent species previously detected in comets, while red points denote species not previously detected, demonstrating the dramatic increase in known hydrocarbons provided by Rosetta. Figure created using data from [127] and based on Figure 8 from [65].

3.9.1. CN

Emission from the CN radical is a very bright, nearly ubiquitous feature in cometary spectra at optical wavelengths and has been observed since spectra of comets were first obtained in the 1800's [25–27,129]. CN has also been observed in the NIR, though interpretation of these emissions in terms of abundances has been limited [75]. As a radical species, it is not inherently present in the nucleus, but is released into the coma via photodissociation of a more complex organic. The leading candidate for this molecule is HCN, though other molecules such as C₂N₂ and HC₃N have been suggested, even though currently, there are little observational data constraining the abundances of these species in cometary comae [130]. While HCN can explain the abundance of CN in many comets (e.g., [23]), there are examples of comets where the CN abundance exceeds that of HCN, and therefore HCN cannot account for all the observed CN (e.g., [74,75]). In these cases, the sublimation of carbon-rich dust grains or CHON particles is often invoked. While CN is easily detected in comets, the lack of knowledge of its origin hinders interpretation of its abundance in terms of nucleus composition.

Due to its intrinsic brightness, CN optical emission has been a favored target for studies of the carbon and nitrogen isotopic ratios in comets, and is the most efficient way to determine isotopic ratios in cometary organic matter via remote sensing. High spectral resolution ($\lambda/\Delta\lambda > 30,000$) is required to separate ¹³CN and C¹⁵N emission lines from the main isotopologues (see Figure 10). The ¹²C/¹³C ratio in cometary CN is ~90, in line with the Earth and other Solar System objects (including Stardust samples and IDPs), suggesting a common carbon reservoir for the formation of organic matter in the Solar System. However, the ¹⁴N/¹⁵N ratio in comets is lower than the Earth by a factor of two and lower than the protosolar value by a factor of three [35]. The reason for this variability in the Solar System is not fully understood, but could be related to different nitrogen reservoirs with

distinct isotopic ratios due to the isotope-selective photodissociation of N_2 in the protosolar disk [131–133].

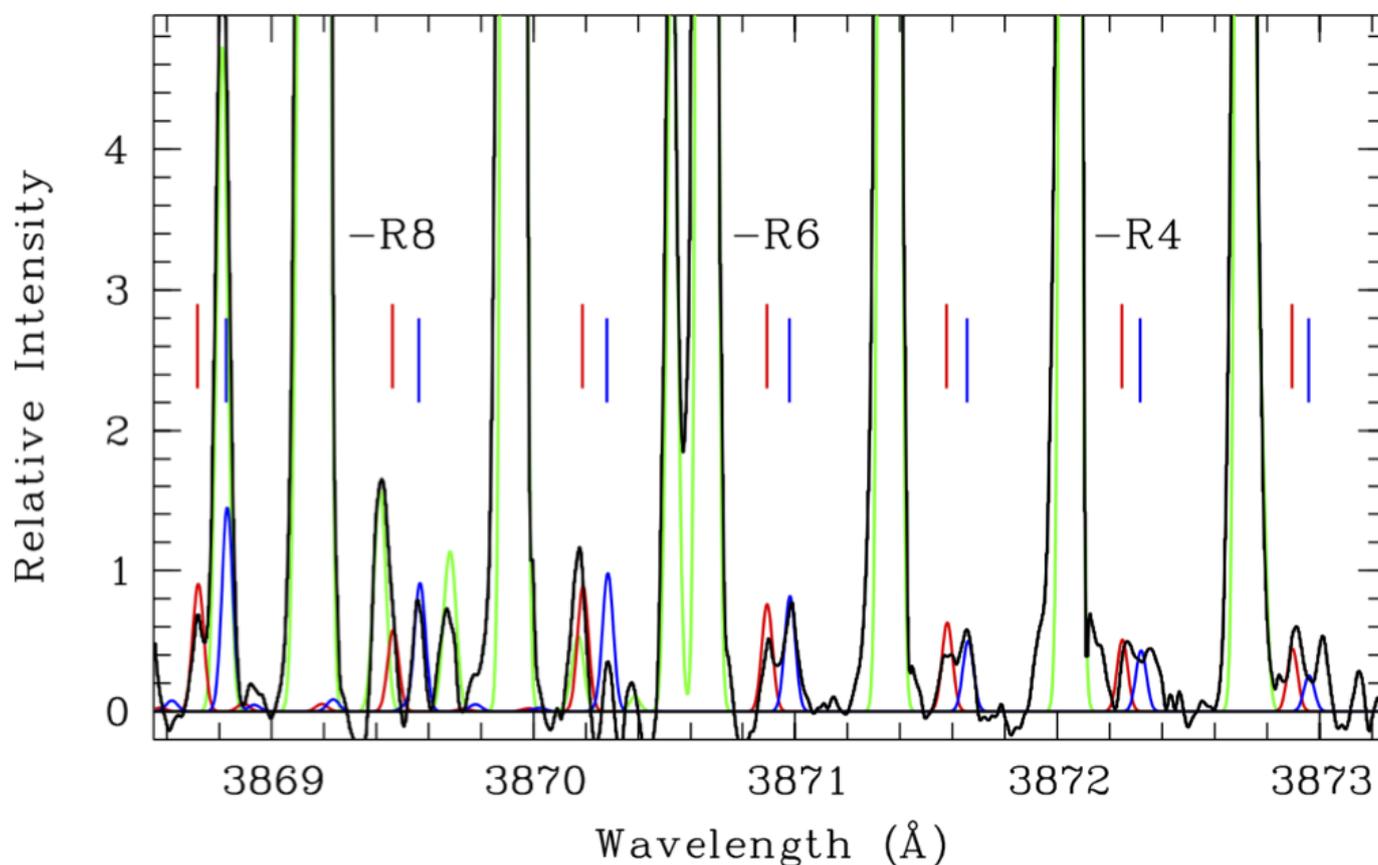


Figure 10. High spectral resolution optical spectrum showing individual CN lines, both of the main isotopologue as well as ^{13}CN and $C^{15}N$. The data are shown in black, with model fits to the observed emission for the main isotopologue (green), ^{13}CN (blue), and $C^{15}N$ (red) overplotted. The R8, R6, and R4 labels indicate the rotational designation for the observed lines. This demonstrates the necessity and power of high spectral resolution for isotopic studies of CN at optical wavelengths. Figure from [134].

3.9.2. C_2

C_2 emission is another very bright feature in the optical spectra of comets, with several bands of the Swan system dominating emission at optical wavelengths. The presence of C_2 in comets has been known for as long as CN, yet its true source still remains a mystery. The leading simple organic parent molecule is C_2H_2 , yet in most comets, C_2H_2 is less abundant than C_2 and cannot account for all the observed C_2 (e.g., [23]). While C_2H_6 is often more abundant than C_2 , the time scale for photodissociation of C_2H_6 to result in C_2 release is much too slow to be a significant source of C_2 [9,33]. Therefore, like CN, CHON particles/carbon-rich dust grains are often cited as the source of C_2 [22,23,75]. If accurate, this would make C_2 emission a bright, easily accessible proxy for tracing complex hydrocarbons/organic matter in comets. However, the current knowledge of the origin of C_2 and how this relates to the abundances of C_2H_2 , C_2H_6 , and other hydrocarbons in comets make the analysis of this nature uncertain.

Studies of C_2 in comets and comparison to CN have revealed that about 1/3 of comets are depleted in C_2 compared to CN [29,30]. These comets are termed “carbon-chain depleted”, as C_2 is expected to trace carbon-chain species. About 2/3 of the depleted comets are JFCs. This may be connected to the relative depletions of the hydrocarbons C_2H_2 and C_2H_6 observed in the IR (see Sections 3.4 and 3.6), but there is no evidence that a comet depleted in C_2 is always depleted in C_2H_2 and/or C_2H_6 as well. The meaning of the

optical taxonomy of comets based on C_2 requires a more complete knowledge of the origin of C_2 in cometary coma.

3.9.3. C_3

Emission from C_3 was identified along with C_2 and CN in the earliest optical spectra of comets [27], though its true nature eluded identification until the mid-20th century [135]. For this reason, its main emission band at 405 nm is called “the Comet Band”. Very little is known about the nature of C_3 release in cometary comae. The best molecular candidate is C_3H_4 (propyne), though like the case of C_2H_6 and C_2 , this is not likely to be a dominant parent [33]. As with C_2 , CHON particles/carbon-rich dust grains are a possibility. However, it seems that there is not a simple origin that explains the presence of C_2 and C_3 in cometary comae, as the abundances of C_3 and C_2 do not always correlate (i.e., some comets are depleted in C_2 but have normal C_3 abundances and vice versa) [29,30]. Much more work is needed to understand the origin of C_3 in cometary comae.

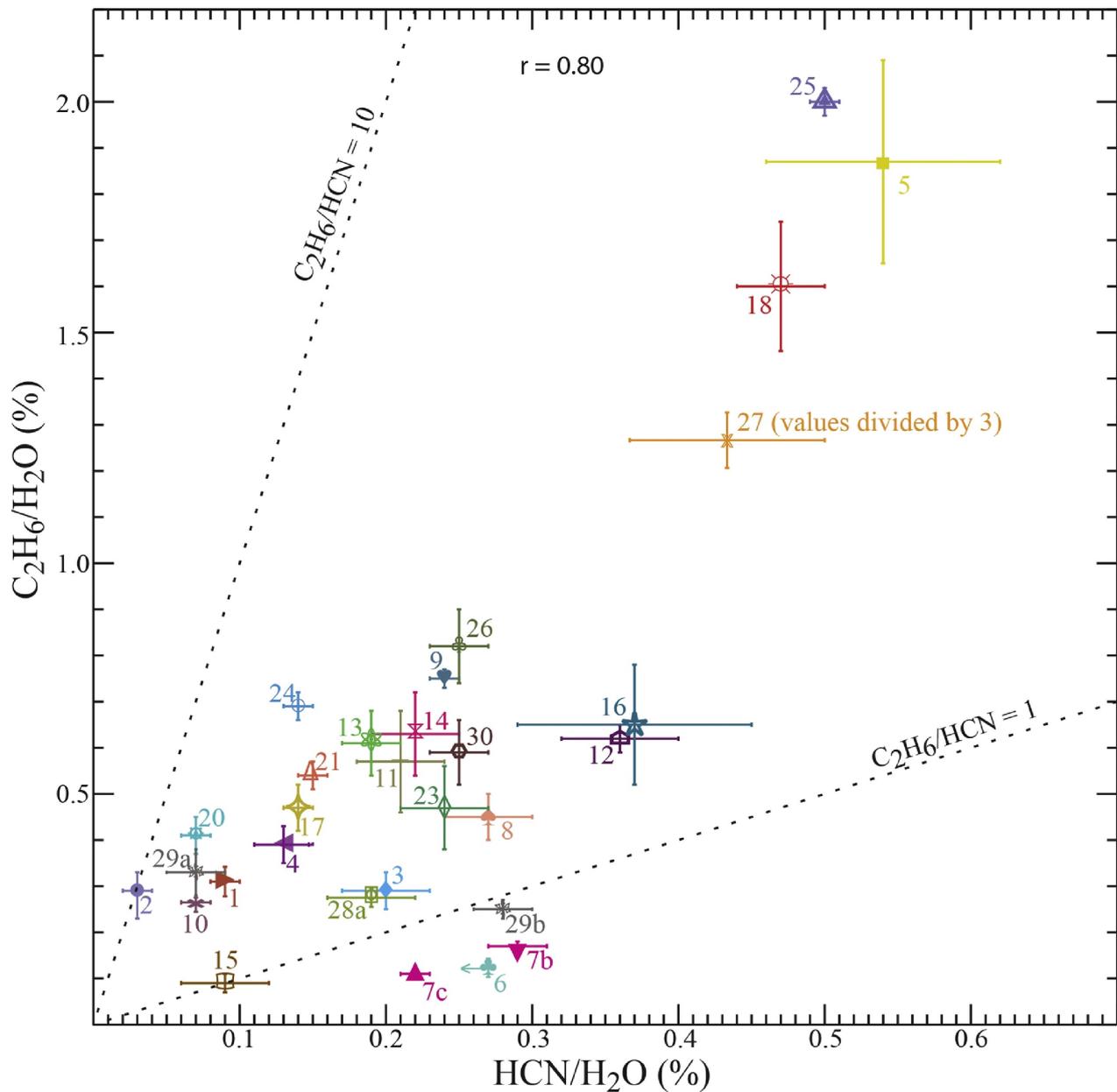
3.9.4. CH

Emissions from CH are harder to detect than CN, C_2 , and C_3 due to the main band observable at optical wavelengths being intrinsically weaker. Therefore, the literature of CH observations in comets is less extensive than these other species, though its presence has been known in comets for nearly as long [136]. The current state of knowledge of CH parentage is similar to C_3 : CH_4 is suggested as a possible parent molecule, though CH release from CH_4 photodissociation is a very inefficient process. Like the other radical species discussed in this section, CH release from CHON particles/carbon-rich dust grains is a possibility, but has not been studied in any detail.

4. Implications

Remote sensing observations at a variety of wavelengths have revealed a number of organic molecules present in comets. The presence of these relatively simple organic molecules hinted at the potential presence of more complicated species, a supposition confirmed by the Rosetta mission, which greatly expanded the list of known organic molecules in comets. Apart from providing an inventory of organic molecules, these results also have implications for the origin and formation of organic matter, as well as their potential delivery to the terrestrial planets.

Many of the simple organic molecules, such as C_2H_6 , H_2CO , and CH_3OH , are efficiently formed via hydrogen addition reactions on grain surfaces involving C_2H_2 and CO. The relative abundances of these species in comets show evidence for this formation mechanism in the protosolar disk. While CO/ H_2CO / CH_3OH ratios show a large scatter suggesting variable efficiency in hydrogenation of CO (or a large role of evolutionary/sublimation effects on observed abundances), C_2H_6 / C_2H_2 ratios are more constant and suggest a very efficient hydrogenation process for C_2H_2 on grain surfaces, if this is indeed the formation process for C_2H_6 in the protosolar disk [8]. Correlations between the abundances of different organic molecules and mapping of spatial distributions in the coma can reveal links between the formation of different organic molecules and their collocation in the nucleus. HCN is highly correlated with hydrocarbons, specifically C_2H_6 , and these species often have similar spatial distributions when observed in the IR, suggesting a common release mechanism from the nucleus (see Figure 11) [8]. Species like H_2CO and CH_3OH show weaker correlations and different spatial distributions, often indicative of an extended source of production ([8,48], see also Figures 4 and 7). These correlations (or lack thereof) could therefore indicate different ice phases in the nucleus (for instance apolar vs. polar, see Section 3.4), and how the organic molecules segregate into these different ice phases could have ramifications for their formation and incorporation into cometary nuclei.



- | | | |
|---------------------|-----------------------------|--------------------------|
| 1. ► 2P/Encke | 10. × 8P/Tuttle | 20. ⚙ C/2003 K4 LINEAR |
| 2. ● 6P/d'Arrest | 11. + 153P/Ikeya-Zhang | 21. △ C/2004 Q2 Machholz |
| 3. ◆ 9P/Tempel 1 | 12. ◻ C/1995 O1 Hale-Bopp | 22. □ C/2006 M4 SWAN |
| 4. ◄ 10P/Tempel 2 | 13. ⚙ C/1996 B2 Hyakutake | 23. ◇ C/2006 P1 McNaught |
| 5. ■ 17P/Holmes | 14. ⌘ C/1999 H1 Lee | 24. ○ C/2007 N3 Lulin |
| 6. ♣ 21P/G-Z | 15. □ C/1999 S4 LINEAR | 25. ▲ C/2007 W1 Boattini |
| 7b. ▼ 73P/SW3-B | 16. ⚙ C/1999 T1 McN-Hartley | 26. ⚙ C/2009 P1 Garrard |
| 7c. ▲ 73P/SW3-C | 17. ◆ C/2000 WM1 LINEAR | 27. × C/2010 G2 Hill |
| 8. ♠ 81P/Wild 2 | 18. ⚙ C/2001 A2 LINEAR | 28. ◻ C/2012 F6 Lemmon |
| 9. ♥ 103P/Hartley 2 | 19. ⚙ C/2002 T7 LINEAR | 29. ⚙ C/2012 S1 ISON |
| | | 30. ◻ C/2013 R1 Lovejoy |

Figure 11. Abundances of C₂H₆ plotted versus HCN abundances in the sample of comets measured at IR wavelengths. The abundances show a fairly strong positive correlation, suggestive of a common release mechanism. Figure from [8].

Several species (in addition to the known photochemical products observed at optical wavelengths discussed in Section 3.9) have distributed sources in cometary comae, including H_2CO , HNC, and sometimes CH_3OH . While for CH_3OH this may point to incorporation of this molecule into water-rich ice grains [96,97,99], the distributed sources for H_2CO and HNC point to a more complex progenitor contained in the cometary dust ([48,49] Sections 3.1 and 3.2). Understanding the nature of these distributed sources can yield clues to the nature of complex organic material in cometary dust grains.

The organic content of comets suggests they could be an important source of the Earth's current biosphere. Using the measurements of organic matter in comet 67P by Rosetta, Rubin et al. 2019 [137] and Altwegg et al. 2019 [65] argued that comets could account for all of the organic material currently present in Earth's biosphere.

The presence of complex organic matter in comets suggests that these molecules form readily in protoplanetary disks and/or the ISM. The organic inventory of comets exceeds the complexity of the ISM, which could point to interstellar inheritance as an origin for some Solar System ices. In particular, the presence of glycine in both Rosetta observations and the Stardust samples suggests amino acids can form in a protoplanetary disk/ISM environment.

5. Future Directions for the Study of Cometary Organic Matter

Both remote sensing observations and directed missions to comets have provided unique insights into cometary organic matter, and both types of studies continue to be vital to provide further understanding. Remote sensing observations are limited to simpler organic molecules, but provide the statistical sampling needed to understand the cometary population as a whole. On the other hand, space missions provide detailed analysis of a specific target, quantifying organic matter that can currently only be detected by being in close proximity (e.g., glycine).

Future missions to comets will build upon the success of Rosetta and Stardust. Comet Interceptor is an ESA mission that will perform a flyby of either a dynamically new (first passage through the inner Solar System) or interstellar object to be determined, providing the first close up study of any comet in either of these dynamical classes, though as a flyby it will be more limited in the scope of its investigations than Rosetta [138]. The next major step in the study of cometary organic molecules is to build off the success of Stardust and Philae and return a sample of material directly from the cometary surface, preferably through a cryogenic sample return, in order to preserve the structure of the nucleus ices. The Comet Astrobiology Exploration Sample Return (CAESAR) was a proposed mission to the Rosetta target comet 67P in order to obtain a sample from the surface and bring it back to Earth. This mission was a finalist in the latest call for NASA New Frontiers Class proposals but was not selected. A similar mission concept called AMBITION has been proposed as part of ESA's Voyage 2050 program [139]. There is no currently selected cometary sample return mission planned for launch, cryogenic or otherwise. In the meantime, analysis of the vast amount of data obtained by Rosetta will continue, providing new insights into the composition of cometary organic matter.

The next generation of remote sensing facilities will provide similar leaps forward in our understanding of cometary organic matter. ALMA has already provided detailed studies of species such as H_2CO , CH_3OH , and HCN, and will continue to do so. Sub-mm observations to search for the more complicated organic molecules detected by ROSINA will be able to identify different isomers (for instance dimethyl ether (CH_3OCH_3) and ethanol), which could not be differentiated with ROSINA. The iSHELL instrument on the NASA IRTF has provided similarly vast improvements in the ability to quantify the composition of comets at IR wavelengths. The next generation of 30-m class telescopes will extend remote sensing observations of cometary volatiles to much fainter targets than currently possible. The James Webb Space Telescope (JWST) will be able to observe the aromatic and aliphatic C–H stretch transitions from hydrocarbons in the 3.3–3.4 micron region [140]. Recent observations of the interstellar comet 2I/Borisov gave us our first insight into the

organic composition of comets from other star systems. While some deviations from Solar System comets have been noted (C_2 depleted, CO enriched), 2I/Borisov is overall fairly similar [141–144]. With survey telescopes such as the Vera Rubin Observatory going online in coming years, more opportunities to discover and characterize the organic composition of interstellar comets should follow with more new discoveries.

Specific avenues for further study include (but are not limited to):

(1) Release of organic matter into the coma. Past results at IR and sub-mm wavelengths have shown that while many organic molecules are released directly from the nucleus (C_2H_6 , HCN), others have a distributed source. H_2CO has a wide range of abundances in comets, and ALMA observations have shown distributed sources for multiple comets to date. Further observations are needed to understand H_2CO abundances in comets and how they connect to more complex organic matter such as POM, CHON particles, or polymers. Similarly, the origin of HNC is not well understood, though it is clear that it is not released directly from the nucleus. The identity of the CH_3OH extended source observed for some comets also warrants further study. A detailed study of the scattering properties of dust grains can also reveal the presence of organic matter [145,146].

(2) Further development of compositional taxonomies. While the optical taxonomy [29,30] has a large sample size (>200 comets), its meaning for the organic composition of comets is not well understood due to a lack of knowledge of the origin of the observed radicals. On the other hand, IR and sub-mm abundance patterns are more straightforward to interpret, but suffer from small sample sizes (~50). While trends are emerging [8], the recent discovery of C/2016 R2 (PanSTARRS), a comet dominated by CO with high N_2 and low H_2O abundances [147–151], has revealed that there is still much that is not understood about cometary composition. More observations at all wavelengths are needed to better interpret compositional taxonomies and what they imply about the organic composition of cometary nuclei.

(3) Cryogenic sample return. The next giant leap in the study of cometary organic matter will be the return of a (preferably cryogenic) sample to laboratories on Earth through a mission such as AMBITION, as discussed above. This will enable the detection and characterization of complex organic matter that has been measured in meteorites, but will only be studied in comets through a sample that is returned to Earth.

Comets are rich in organic matter and are vital tools to understanding the formation of organic matter in the ISM/protosolar disk and subsequent delivery to the terrestrial planets. Past studies have revealed much about the organic inventory of comets, and the future is bright for continued insights into the organic composition of cometary nuclei.

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Appendix A

This appendix includes individual comets observed after 2015 that we included in Table 1 and were not included in the previous compilations of Dello Russo et al. 2016 [8] and Bockelee-Morvan and Biver 2017 [67]. For the statistics for results published prior to 2015, we refer the reader to these works. Any species present in Table 1 but not below do not have any new ground-based observations reported since 2015. Blank columns indicate that no new observation (i.e., since 2015) for that species in that particular comet is available. For comets with a range of values from different works, we used the average of these values when calculating mean values for the population. In addition to the species below, Rosetta quantified the following species that have been detected remotely in other comets: $\text{HNCO}/\text{H}_2\text{O} = 0.027\%$, $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 0.006\%$, $\text{HC}_3\text{N}/\text{H}_2\text{O} = 0.0004\%$, $\text{HCOOH}/\text{H}_2\text{O} = 0.013\%$, $\text{HCOOCH}_3/\text{H}_2\text{O} = 0.003\%$, $\text{CH}_3\text{CHO}/\text{H}_2\text{O} = 0.047\%$, $(\text{CH}_2\text{OH})_2/\text{H}_2\text{O} = 0.011\%$, $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O} = 0.039\%$, $\text{NH}_2\text{CHO}/\text{H}_2\text{O} = 0.004\%$, and $\text{H}_2\text{CS}/\text{H}_2\text{O} = 0.0027\%$ [137,152,153].

Table A1. Table detailing abundances observed in individual comets since 2015 that were included in the tabulation of Table 1

Comet	Abundance (X/H ₂ O in %)						
	HCN	HNC	C ₂ H ₂	CH ₄	C ₂ H ₆	H ₂ CO	CH ₃ OH
2P/Encke [110]	0.12			0.11	0.04	0.27	0.87
21P/Giacobini-Zinner [111,114]	0.15			1.1	0.23		2.3
45P/Honda-Mrkos-Pajdušáková [52,113]	0.05–0.15		0.08	0.79–1.0	0.52–0.81	0.14–0.36	3.6–4.5
46P/Wirtanen [154]	0.09						
67P/Churyumov-Gerasimenko [108,127,137,153]	0.14			0.34–0.47	0.29	0.32	0.21
252P/LINEAR [155]	0.23				0.95		4.9
C/2012 F6 (Lemmon) [156]	0.06	0.003				0.1	0.97
C/2012 K1 (PanSTARRS) [50,157]	0.14			0.46	0.87		1.7–2.7
C/2012 S1 (ISON) [75,156,158]	0.11–0.26	0.05	0.21	0.33	0.29	0.23–1.1	0.49–1.4
C/2013 R1 (Lovejoy) [159]	0.2						
C/2013 V5 (Oukaimeden) [107]	0.08		0.07	0.28	0.2	0.13	0.95
C/2014 Q2 (Lovejoy) [159,160]	0.09					0.2	2.2
C/2017 E4 (Lovejoy) [161]	0.17		0.14	0.34	0.39	0.36	1.62

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