

Distributed Sources in Comets

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Abstract The distribution of some molecules and radicals (H_2CO , CO , HNC , CN , ...) in the atmosphere of several comets cannot be explained only by a direct sublimation from the nucleus, or by gas phase processes in the coma. Such molecules are in part the result of a distributed source in the coma, which could be the photo and thermal degradation of dust. We present a review of the degradation processes and discuss possible interpretations of the observations in which the degradation of solid complex organic material in dust particles seems to play a major role. The knowledge of such gas production mechanisms provides important clues on the chemical nature of the refractory organic material contained in comet nuclei.

Keywords Comets · Distributed source · Extended source · Composition · Organic chemistry · Modelling

Introduction

Our current knowledge of the composition of the comet nuclei derives from observations made in their atmospheres, and from our understanding of the physico-chemical processes governing the emission of material into the atmosphere (sublimation of ices contained in the nucleus releasing gaseous molecules and dragging along solid particles), and its evolution once out-gassed or lifted. Recently, Stardust spacecraft captured cometary grains in the atmosphere of Comet 81P/Wild 2. Those grains were brought back to Earth in 2006 and were analysed in the laboratory where it has been shown they were made of a complex mineral and organic mixture (Brownlee et al. 2006). The grains collected during this mission are representative of the most refractory component of comets, emitted from the nucleus, that survived the collection process. Until the *Rosetta* mission succeeds in landing the *Philae* probe at the surface of Comet 67P/Churyumov–Gerasimenko in 2014, the only way to study

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the whole unaltered molecular composition of cometary nuclei will be in an indirect way, reconstructing the composition of the nuclei from what we can probe in their atmospheres.

The simplest way to describe chemistry within cometary atmospheres is the application of Haser's model which supposes that 'parent molecules' are released only by the nucleus ices sublimating and that 'daughter molecules' are produced solely by the photodissociation of a single gaseous species. Moreover, this simple model requires many hypotheses: radial expansion of molecules at constant velocity, stationary state of the gas production, spherical symmetry around the nucleus, and destruction of the 'parent' species by photodissociation (Haser 1957). More advanced hypothesis have to be introduced into models to take into account a chemistry more elaborated than simple photolysis (proton transfer, dissociative recombination, etc.), and more elaborated physics than radial transport at constant velocity (hydrodynamic models, magnetohydrodynamic & Monte Carlo models (Rodgers et al. 2004; Ip 2004; Combi et al. 2004)). However, approaching the distribution of parent molecules in comets via a Haser distribution is usually sufficient, while the study of species formed in the coma requires the other kind of modelling.

The present paper focuses specifically on distributed sources, also called sometimes 'extended' sources in the literature. Properly speaking, this term could apply to any compound formed in the coma from a parent molecule by any kind of process (photolysis, electron impact, charge exchange reactions, dissociative electron recombination...). However, such mechanisms are considered as normal coma chemistry, and do not require the introduction of an additional term. In common cometary terminology, the use of "distributed sources" or "extended sources" can be confusing as it is not really associated to a clear and self-consistent definition. It often refers to the production of a molecule in the coma through an unknown process, with no associated known parent. In the book *Comets II* (Festou et al. 2004), the following definition is given in the glossary:

Extended source – Most stable molecular species (as opposed to radicals, atoms and ions) appear to be emitted directly from the nucleus. Some stable molecular species appear to have at least one component that is produced in the coma from another source. Processes that have been suggested are sublimation from grains or large polymerized molecules, photon-induced desorption or photo-sputtering from grains or large molecules, gas-phase chemistry in the coma, or photodissociation of other parent molecules. Well known examples in comets are extended source components of H_2CO and CO . The term "distributed source" is also often used.

We do not endorse this definition as it excludes radicals while CN , C_2 and C_3 radicals are also often associated with a distributed source, and including these species in the present definition would also include any compound produced in the coma through the mechanisms mentioned above. Moreover, the term "extended source" is rather ambiguous as it is also used to describe the extended nature of the gas and dust release across the nucleus surface (for example in Thomas et al. 1988). This problem is clarified by using the word *distributed*. It also makes sense to favour this term since it is the common mathematical word used to describe inhomogeneous terms in differential equations, e.g., the right-hand-sides of the conservation equations presented later in this paper. Therefore, using the word *distributed* causes less confusion and is more consistent with common science/mathematics usage.

Taking into account the previous discussion, we propose the following definition:

A *distributed source* is an additional source of a gaseous species being produced in the coma from the grains. It is an exchange of mass between the dust and the gas inventory of the coma. Henceforth, we restrict the expression "distributed source" to the production of gaseous species in the coma from solid materials. In this usage, mechanisms that simply

change one gaseous molecule to another, keeping the mass budget unchanged, are understood as chemistry, and not distributed sources. We propose the use of the term “secondary source” in this case as opposed to distributed to avoid any confusion and the use of “additional source” to cover both distributed and secondary sources. The present definition of the distributed sources seems rather consistent, for future use and with its historical use in the literature. Of course, it may not be known from observations alone whether an enhancement in the density of a species in the coma is due to a dust (distributed) source, but such a situation can't be avoided at present.

To date, the origins of observed species tagged as “distributed” are unknown or at least uncertain. The first section of this paper is a review of the observations of distributed species while interpretations of these observations are discussed in the second section.

1 Observations

The best way to reveal the origin of the production of a gaseous species detected in the atmosphere of a comet, and whether it is directly released from the nucleus, produced by chemistry in the gas phase, or by a distributed source, is to determine its radial distribution in the coma. Moreover, to make a distinction between a production by chemistry or a distributed source, the spatial distributions have to be carefully analysed. In some cases, densities of gaseous species as a function of the distance from the nucleus were measured in-situ by mass spectroscopy. This technique has revealed for the first time the existence of distributed sources in the coma of Comet 1P/Halley (Meier et al. 1993). Nevertheless, the spatial distribution of gas species is generally determined by long-slit spectroscopy at infrared, visible and ultraviolet wavelengths as well as by coarse mapping or interferometry at millimeter wavelengths (Bockelée-Morvan et al. 2004).

Others observational clues on the existence of distributed sources can be found. Indeed generally, the heliocentric evolution of the production rates of molecules produced by a distributed source is steeper than the one of molecules produced from the nucleus (Bockelée-Morvan and Rickman 1997). Moreover, the line shape at millimeter wavelengths, which is characteristic of the motion of gas species in the coma, could give clues on the production mechanism (Gunnarsson et al. 2002; Womack et al. 1997).

In this chapter, we review the observational evidences for some of the distributed source for H_2CO , CO , HNC , CN and some sulfur compounds. Concerning C_2 and C_3 radicals, for which the nature of the parents is uncertain, some information can be found in Combi and Fink (1997), Festou (1999) and Helbert et al. (2005).

1.1 Distributed Source for H_2CO

The radial distribution of H_2CO in the coma of 1P/Halley has been deduced from in-situ measurements by the Neutral Mass Spectrometer (NMS) onboard the Giotto spacecraft (Meier et al. 1993; Eberhardt 1999). It has been shown that its density profile cannot be reconciled with its only source in the nucleus. The additional source for the H_2CO production has been confirmed by coarse mapping at radio wavelengths in Comets C/1990 K1 (Levy), C/1989 X1 (Austin) (Colom et al. 1992) and C/1996 B2 (Hyakutake) (Biver et al. 1999). In Comet C/1995 O1 (Hale-Bopp), interferometric observations have also shown that H_2CO had an additional source (Wink et al. 1997; Bockelée-Morvan and Crovisier 2000; Milam et al. 2006). All these observations suggest that the production scale length for H_2CO is about 7000 km at 1 AU, which does not fit with the photodissociation of any known

possible gaseous parent (see Sect. 2). These observations have been performed for heliocentric distances lower than 1.5 AU. Moreover, the H₂CO production rates measured in C/1995 O1 (Hale-Bopp) present a very steep heliocentric evolution which suggests that the origin of some H₂CO is distributed out to 4 AU (in and outbound) (Biver et al. 2002a; Bockelée-Morvan and Rickman 1997).

1.2 Distributed Source for CO

In a similar manner than for H₂CO, an additional and potentially distributed source for CO has been discovered in the coma of 1P/Halley thanks to in situ measurements by mass-spectrometry (Eberhardt et al. 1987; Eberhardt 1999). These measurements indicate that approximately one third of the total CO is produced directly from the nucleus, while the remainder of CO comes from an additional source located in the innermost 25 000 km of the coma (Eberhardt 1999). Determination of the CO spatial distribution by infrared long-slit spectroscopy has confirmed the existence of a CO additional source in Comet C/1996 B2 (Hyakutake) (DiSanti et al. 2003). This observation suggests a parent scale length of about 1000 km and a release rate from nucleus that accounts for about 80% of total observed CO. A coarse map of the CO spatial distribution has also been obtained at millimetre wavelengths in this comet (Biver et al. 1999). Both observations are compatible with most of the CO being released from the nucleus, at least within the innermost 1000 km in the coma. As these observations do not extend farther than 7000 km in the coma, they are not sensitive to other sources with a scale length as large as the one observed in Comet 1P/Halley. In Comet C/1995 O1 (Hale-Bopp), the spatial distribution of CO has been determined by infrared long slit spectroscopy by numerous authors (Brooke et al. 2003; Disanti et al. 2001, 1999; Weaver et al. 1997) for heliocentric distances smaller than 2 AU. These observations suggest that the production of additional CO reaches its terminal value at a distance of about 7000 km from the nucleus at 1.49 AU and 5000 km at 1.06 AU (Brooke et al. 2003; Disanti et al. 2001). The ratio of nucleus to additional sources release rates determined from these infrared observations remains controversial. Indeed, according to different authors, the release of CO from additional source could represent 50% (Disanti et al. 2001) or 90% (Brooke et al. 2003) of the total. Beyond 2 AU from the Sun, only the nucleus source was seen by infrared long slit spectroscopy (Disanti et al. 2001). Nevertheless, this observation seems to be contradictory with the ones performed in the radio domain, which probe larger fractions of the coma than the infrared observations. The radio observations show that at large heliocentric distances, the profiles of the CO radio lines in Comet C/1995 O1 (Hale-Bopp) could be fitted assuming a production by a distributed source (Gunnarsson et al. 2003). Interferometric maps of the CO spatial distribution have been obtained when the comet was close to perihelion (Henry et al. 2002). They show strong deviations from those expected for an isotropic distribution of CO, probably caused by the existence of CO jets. One may also note that the heliocentric evolution of the CO production rates in Comet C/1995 O1 (Hale-Bopp) is not as steep as for H₂CO, HNC or CS (Biver et al. 2002a) as one might expect from distributed sources. First coarse mapping at millimeter wavelengths of CO in Comet 29P/Schwassmann–Wachmann 1 at 6.2 AU seems to reveal a strong additional source at such heliocentric distances (Gunnarsson et al. 2002). Nevertheless, new observations and analysis of the CO line profile indicate that the additional source, if present, is very weak (Gunnarsson et al. 2008). Since the observations seem to be inconsistent, a summary of them is given in Table 1.

Table 1 Summary of the observations of the CO additional source

Comet	References	Observational method	R_H (AU)	Remarks
1P/Halley	Eberhardt et al. 1987	(1)	0.9	<ul style="list-style-type: none"> • Production of CO at $\rho < 20\,000$ km • $Q_{\text{nucleus}}(\text{CO})/Q_{\text{nucleus}}(\text{H}_2\text{O}) = 3.5\%$ • $Q_{\text{total}}(\text{CO})/Q_{\text{nucleus}}(\text{H}_2\text{O}) = 11\%$ • Production of CO at $\rho < 25\,000$ km
	Eberhardt 1999	(1)	0.9	
C/1996 O2 (Hyakutake)	DiSanti et al. 2003	(2)	0.64–1.06	<ul style="list-style-type: none"> • $Q_{\text{nucleus}}(\text{CO}) = 14.9\%$ • $Q_{\text{total}}(\text{CO}) = 19.1\%$ • Production of CO at $\rho < 10^3$ km for $R_H = 0.64$ AU • Production of CO at $\rho < 2-3 \cdot 10^3$ km for $R_H = 1.06$ AU
	Biver et al. 1999	(4)	1.24	
C/1995 O1 (Hale-Bopp)	Weaver et al. 1997	(2)	1.1	<ul style="list-style-type: none"> • Detection of a CO distributed source
	Disanti et al. 1999 and 2001	(2)	0.93–4.11	<ul style="list-style-type: none"> • Detection of a CO distributed source only for $R_H < 2$ AU • $Q_{\text{nucleus}}(\text{CO})/Q_{\text{total}}(\text{CO}) \approx 50\%$ for $R_H < 2$ AU • Production of CO at $\rho < 6-7 \cdot 10^3$ km for $R_H = 1.49$ AU and at $\rho < 5 \cdot 10^3$ km for $R_H = 1.06$ AU
	Brooke et al. 2003	(2)	1.02–1.05	<ul style="list-style-type: none"> • Detection of a CO distributed source • $Q_{\text{nucleus}}(\text{CO})/Q_{\text{total}}(\text{CO}) \approx 10\%$ • $L_P \approx 5000$ km (*)
	Gunnarsson et al. 2003	(3)	3.7–10.8	<ul style="list-style-type: none"> • Detection of a CO distributed source • $Q_{\text{nucleus}}(\text{CO})/Q_{\text{total}}(\text{CO}) \approx 10-60\%$
	Henry et al. 2002 Biver et al. 2002a	(5) (6)		<ul style="list-style-type: none"> • Presence of a spiral CO jet • No steep heliocentric evolution of $Q(\text{CO})$

- (1) In-situ mass spectrometry
- (2) Long slit spectroscopy at infrared wavelengths
- (3) Analysis of the radio line profile
- (4) Coarse mapping at radio wavelengths
- (5) Interferometry at radio wavelengths
- (6) Determination of the production rates at radio wavelengths
- (*) L_P : production scale length of the distributed molecule. See precisions in Sect. 2.1

1.3 Distributed Source for HNC

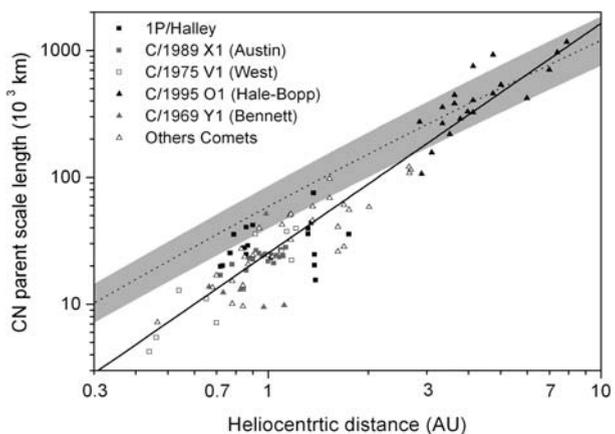
HNC, which is an isomeric form of HCN, was detected for the first time in Comet C/1996 B2 (Hyakutake) (Irvine et al. 1996) at millimeter wavelengths. It was then observed in C/1995

O1 (Hale-Bopp) (Biver et al. 2002a; Irvine et al. 1998a) and in other comets (Biver et al. 2002b, 2006). In Comet C/1995 O1 (Hale-Bopp), interferometric observations made it possible to measure the HNC spatial distribution (Wink et al. 1997), which deviates from that of HCN in the innermost coma, and indicates production of HNC in the coma. Nevertheless, the main indication of an HNC distributed source is the heliocentric dependence of the HNC/HCN ratio. Indeed, as for the H₂CO production rates, this ratio increases with decreasing heliocentric distance in Comet C/1995 O1 (Hale-Bopp) (Biver et al. 2002a), C/2002 C1 (Ikeya-Zhang) (Irvine et al. 2003) as well as for other comets (Biver et al. 2006).

1.4 Distributed Source for CN

Reviews about the existence of the CN additional source have already been published (Festou 1999; Fray et al. 2005). It is clear that at least some of the CN radicals are produced in the coma through HCN photodissociation. Nevertheless, it is not clear if this mechanism could solely explain the abundance of CN. Indeed CN and HCN production rates have the same order of magnitude in most of the comets and considering the uncertainties in their production rates, we cannot conclude if HCN is the only parent molecule of CN or not in most of the comets. In comets, the ¹⁴N/¹⁵N isotopic ratios in CN is about two times lower than on Earth (Hutsemékers et al. 2005). First measurements of the ¹⁴N/¹⁵N in HCN (Jewitt et al. 1997; Ziurys et al. 1999) lead to values close to the terrestrial one. This was a major indication that HCN could not be the unique parent molecule of CN radicals until new measurements in comet 17P/Holmes and reanalysis of the older observations show that the ¹⁴N/¹⁵N isotopic ratio in CN and HCN are about the same (Bockelée-Morvan et al. 2008). Nevertheless, from this new result, we cannot exclude that CN has other major progenitors, than HCN, sharing the same low ¹⁴N/¹⁵N isotopic ratio (Bockelée-Morvan et al. 2008). The spatial distribution of CN has been measured in numerous comets by long-slit spectroscopy at UV wavelengths. From these observations, it seems that CN radicals could be entirely produced by the HCN photodissociation for heliocentric distances greater than 3 AU. Nevertheless, closer to the Sun, the CN spatial distribution is too narrow to be explained only by this process (Bockelée-Morvan and Crovisier 1985; Fray et al. 2005). Indeed for heliocentric distance less than 3 AU, the CN parent scale length is lower than the HCN photodissociation scale lengths (see Fig. 1).

Fig. 1 Measured CN parent scale lengths as a function of the heliocentric distance. The CN parent scale lengths have been normalized to the minimum of solar flux and the *black line* is the best fit to these data. The *dashed line* is the effective CN parent scale length assuming that CN is produced exclusively by photodissociation of HCN. The *grey region* represents the error on the effective CN parent scale lengths due to uncertainties in the photodissociation rate of HCN and in the expansion velocity (figure from Fray et al. 2005)



1.5 Distributed Sources for Other Species

The radial distribution of OCS has been determined in Comet C/1995 O1 (Hale-Bopp) at about 1 AU from the Sun by infrared long-slit spectroscopy (Dello Russo et al. 1998). This observation suggests that about 70% of the total production of OCS comes from an additional source having a parent scale length of 3000–3500 km. The fact that most sulfur is contained in the refractory CHON grains suggests that OCS may be derived from refractory grains by a distributed source. However, as the mechanism for a distributed source for OCS is unknown, an additional contribution from other gaseous species cannot be ruled out.

CS has been observed in different comets at millimeter and ultraviolet wavelengths. The CS/HCN and CS/H₂O production rate ratios increase with decreasing heliocentric distance in all the comets for which CS has been observed (Biver et al. 2000, 2002a, 2006). The spatial distribution of CS has been determined thanks to coarse mapping at millimeter wavelengths in Comet C/1996 B2 (Hyakutake) at 0.7 AU (Biver et al. 1999) suggesting a parent scale length of about 1200 km. Whereas this value is roughly in agreement with the photodissociation scale length of CS₂, which has been tentatively detected in Comet P/122 de Vico (Jackson et al. 2004), the increase of CS abundance with decreasing heliocentric distance suggests that CS is also produced by an additional mechanism (Biver et al. 2006).

In Comet C/1995 O1 (Hale-Bopp), the SO spatial distribution has been measured by interferometry at millimeter wavelengths (Wink et al. 1997). This observation shows clearly that SO is a daughter species. SO is at least produced in part by the photodissociation of SO₂. Nevertheless, its production rate is greater than the one of SO₂, suggesting an additional production mechanism of SO (Bockelée-Morvan et al. 2000; Boissier et al. 2007).

First detection of radical NS is reported in Comet C/1995 O1 (Hale-Bopp) (Irvine et al. 2000). In their paper, the authors state that whether NS itself is present in the nucleus or has a distributed source in the coma is unknown.

2 Interpretations

2.1 General Discussion

Understanding the chemistry of comets is quite a difficult task. The additional sources, including distributed and secondary sources, do not have an origin based on the same mechanism. Some physical and chemical mechanisms which could explain the origin of secondary and distributed (i.e. additional) sources are summarized in Fig. 2. Some production of gaseous species may result from the dissociation (photolysis or other chemical processes including electron impact (Helbert et al. 2005)) of several gaseous parents (among which some may not have been detected to date) or chemistry between two gaseous compounds in the innermost coma. Distributed sources include sublimation of icy grains in the coma or the production of gaseous compounds during the degradation of solid organic material contained in cometary dust particles.

Indeed, it is now established that the organic content of comets is more complex than what is seen in the gaseous phase alone. Most of the detections presented in the above section are all remote sensing observations, probing the gaseous phase of comets, leading to the detection of about 20 stable gaseous molecules (Bockelée-Morvan et al. 2004). However in 1986, Vega 1 & 2 and Giotto spacecrafts probed the atmospheres of Comet 1P/Halley. Molecular analyses of solid particles in the coma were conducted by mass spectrometry and resulted in the detection of solid organic compounds much more complex than the gaseous

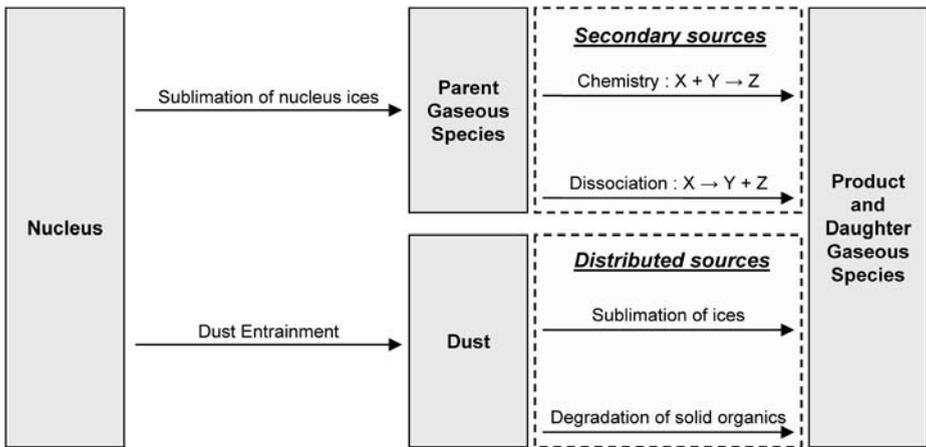


Fig. 2 Chemical mechanisms of production of the gaseous species in the cometary environment. The ‘secondary’ and ‘distributed’ sources have been clearly distinguished

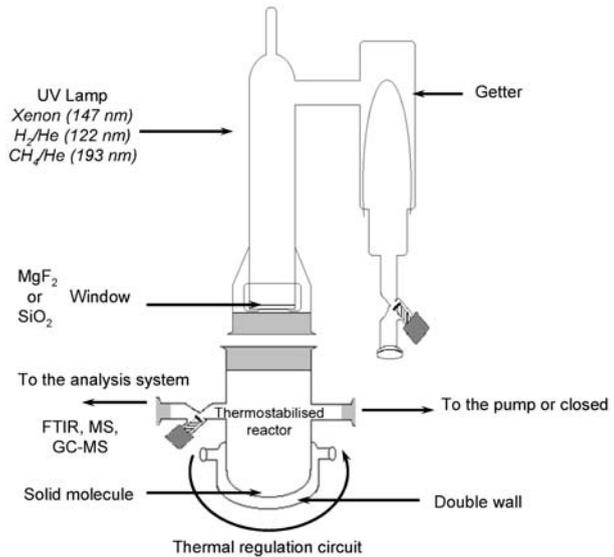
ones securely detected from the Earth. It showed that more organic material is present, in the solid state, and that its molecular mass can reach value above 150 amu (Kissel and Krueger 1987; Mitchell et al. 1992). In-situ results from the Stardust mission (with the CIDA mass spectrometer) have confirmed these observations (Kissel et al. 2004). Recently, the analysis of grains captured from Comet 81P/Wild 2 by the Stardust spacecraft has also enabled the detection of complex organic material made of aliphatic and aromatic hydrocarbons, and molecules bearing a large range of organic functions (hydroxyl, carbonyl, amide, nitrile ...) with high molecular weight (up to 300 amu) (Keller et al. 2006; Sandford et al. 2006).

For an even better insight into the most complex and less volatile material, one can turn to experimental laboratory work. The principle of such experiments is the following: from observations of the most abundant species in comae and in the interstellar medium, one can infer probable compositions of the nucleus ices. A gaseous sample of the key species is condensed under near vacuum conditions on a cold substrate and irradiated by UV photons or charged particles. Sometimes, condensed ices are also simply warmed up slowly without irradiation. These processes are similar to the ones precometary ices may have encountered in the Solar Nebula or in the interstellar medium and they allow the synthesis of complex organic compounds from the initial simple ice. When the sample is warmed up for analysis, a refractory organic residue remains on the substrate at ambient temperature. The diversity of organic compounds synthesized during those experiments is remarkable (Greenberg 1982; Colangeli et al. 2004; Despois and Cottin 2005), and this mixture of molecules can be considered as an analogue of the solid organic component of comets.

In the frame of the study of distributed sources, a new generation of cometary laboratory experiments has been developed. Proceeding in an opposite direction than the ‘classical’ ice experiments, they study the production of gaseous compounds during the photo-degradation (induced by the solar UV flux) and the thermal-degradation (induced by dust particles heating) of complex solid molecules suspected to be present in cometary dust particles, once they are ejected in the coma. Such experiments are described in Cottin et al. (2000), Fray et al. (2004a, 2004b) and an example is given in Fig. 3.

These experiments are not actually meant to *simulate* the cometary environment, but rather to measure physico-chemical data, such as production quantum yields (photo-

Fig. 3 Experimental setup dedicated to the study of the degradation of solid organic material into gaseous fragments. The solid organic molecule is deposited at the bottom of a Pyrex reactor where it can be heated with a thermal regulation circuit or photolyzed (at different wavelengths) with a UV lamp located at the top of the reactor. Gaseous degradation products can then be analyzed by infrared spectroscopy, direct mass spectrometry or gas chromatography coupled with a mass spectrometer (more details in Cottin et al. 1999, 2000)



degradation), Arrhenius constants and activation energies (thermal-degradation), characteristic of the gaseous production resulting from the decomposition of some specific targeted solid material. Results obtained after that kind of experiments, which were not necessarily conducted in a cometary context, are summarized in Table 2.

These quantitative data are then included into numerical models simulating the production of gaseous species during the degradation of solid compounds ejected in the cometary atmosphere on dust particles. The purpose of these models is to calculate the spatial distribution of the gaseous species produced by these mechanisms. With hypotheses similar to the classical Haser's approach, these models are based on the equation of conservation.

If a gaseous species is produced solely by the photodissociation of a unique parent molecule, then the conservation equation can be written:

$$\frac{\partial n_D}{\partial t} + \text{div}(n_D \cdot v_{\text{gas}}) = \beta_P \cdot n_P - \beta_D \cdot n_D. \quad (1)$$

Here n_P and n_D are the number density (m^{-3}) of the parent and daughter molecules respectively, β_P and β_D the photodissociation rates (s^{-1}) of the parent and daughter molecules and v_{gas} the gas expansion velocity in the coma (m s^{-1}) assumed to be constant. In the frame of the Haser's model, the parent (l_P) and daughter (l_D) scale lengths are defined as the product of the gas expansion and the photo-lifetime (reciprocal of the photodissociation rate). The distribution of daughter molecules produced by the photo processes of a single gaseous parent is shown in (2), where Q_P and Q_D are the spherically symmetric production rates of parent and daughter molecules (s^{-1}).

$$n_D(r) = \frac{1}{r^2} \left(\frac{Q_P}{4\pi v_{\text{gas}}} \frac{l_D}{l_P - l_D} (e^{-r/l_P} - e^{-r/l_D}) + \frac{Q_D}{4\pi v_{\text{gas}}} e^{-r/l_D} \right). \quad (2)$$

In most cases, the parent and daughter scale lengths are measured by adjustment of the observations with (2). This parent scale length is then compared to the photodestruction rate of a candidate parent molecule. This comparison gives important clues on the nature

Table 2 Summary of data available on the degradation of potential precursors of distributed sources

	Photodegradation			Thermal degradation		
POM	Products and production quantum yields for various wavelength from Cottin et al. (2000)			H ₂ CO is the only product. Kinetic parameters for its production as a parameters for its production as a function of T (Arrhenius law) for two different POM polymers are given below. From Fray et al. (2004a).		
	λ (nm)	122	147	193	Ea (J mol ⁻¹)	A (molec g ⁻¹ s ⁻¹)
	H ₂ CO	0.75 ± 0.21	0.96 ± 0.19	<0.16	POM 81 × 10 ³	1.2 × 10 ³⁰
	HCOOH	0.13 ± 0.05	0.26 ± 0.10	ϵ	1 ± 0.76%	+28%/-22%
	CO	NE	~ 1	ϵ	POM 99 × 10 ³	7.2 × 10 ³²
	CO ₂	NE	~ 0.3	ϵ	2 ± 2.3%	+140%/-60%
	CH ₃ OH	~ 0.05	~ 0.05	ϵ		
	<i>NE : Present but not estimated</i>					
HMT	Some HCN detected at 147 nm but at level too low to be quantified (Cottin et al. 2002)			No thermal degradation. HMT sublimates when heated under vacuum (Fray 2004)		
HCN polymer	Some HCN, CH ₄ and C ₂ H ₂ are produced with quantum yields lower than 0.03 at 122 and 147 nm (Fray 2004; Fray et al. 2004b)			NH ₃ and HCN are the major products of the thermal degradation (Fray et al. 2004b). The production kinetics have been measured for $T > 420$ K (Fray 2004). Nevertheless, for lower T , the production declines to very low value (unpublished results)		
C ₃ O ₂ polymer	No data available			For $T > 400$ K: release of CO ₂ For $T > 500$ K: increased efficiency in the degradation, with release of CO ₂ and CO. CO/CO ₂ ratio increases with T . From Blake and Hyde (1964) and Smith et al. (1963)		

of the gaseous parent molecule. Nevertheless, one should keep in mind that the ejection velocity acquired by the daughter species during the photolysis of the parent is neglected. This actually changes the physical meaning of the parent scale length (Combi and Delsemme 1980), but as a first approximation this results in estimations usually sufficient to suggest a possible parent.

In the case of a production from the degradation of solid material in cometary dust particles, the conservation equation is:

$$\frac{\partial n_D(r)}{\partial t} + \text{div}(n_D(r) \cdot v_{\text{gaz}}) = (n_{\text{grain}}(r) \cdot \sigma_\alpha(r) \cdot C_D) + (n_{\text{grain}}(r) \cdot m_\alpha(r) \cdot k_D(T)) - (\beta_D \cdot n_D(r)). \quad (3)$$

In the right side of this equation, the first two terms are the production of the considered gaseous species by the photo- and the thermal-degradation of the solid material. In this equation, n_{grain} is the grain density in the coma (m⁻³), σ_α the surface of material exposed to the

Solar flux and C_D the production rate of gaseous species by photo-degradation ($m^{-2} s^{-1}$), m_α the mass of solid material in each particles and k_D the production rate of the gaseous species by thermal-degradation ($kg^{-1} s^{-1}$).

With classical Haser's hypotheses regarding the dynamics in the coma, two scale lengths related respectively to the thermal- (l_T) and photo-degradation (l_P) can be defined (Cottin et al. 2004; Fray et al. 2006) and (3) is integrable analytically. Then, n_D can be written:

$$n_D(r) = \frac{1}{4\pi r^2 v_{gas}} \left\{ \frac{3Q_{grain}\beta^3 m_\alpha}{m_D l_T X} \left[\begin{aligned} & l_D(1-X)(1 - e^{-\frac{r}{l_D}}) \\ & + \frac{(3X-2)(1+1/\beta)}{(1/l_D-1/l_T)} (e^{-\frac{r}{l_T}} - e^{-\frac{r}{l_D}}) \\ & + \frac{(1-3X)(1+1/\beta)^2}{(1/l_D-2/l_T)} (e^{-\frac{2r}{l_T}} - e^{-\frac{r}{l_D}}) \\ & + \frac{X(1+1/\beta)^3}{(1/l_D-3/l_T)} (e^{-\frac{3r}{l_T}} - e^{-\frac{r}{l_D}}) \end{aligned} \right] + Q_D e^{-\frac{r}{l_D}} \right\}. \tag{4}$$

Where Q_{grain} is the production of grains of a specific size and composition, β is the ratio l_T/l_P , m_D the mass of the daughter molecule, X is related to the photoproduction of the daughter compound, and Q_D the contribution from the nucleus to the production of the molecule (more details can be found in Cottin et al. (2004)).

Even if this equation can be simplified in the case that either thermal or photo degradation is not relevant (one being negligible compared to the other), (4) has to be integrated over the whole size distribution of dust particles, taking into account the velocity and temperature for each size range. Moreover, the scale lengths related to the degradation of solid material depend on the initial composition of the cometary dust particles: they are not characteristic for a specific solid material. Therefore, parent scale length, as the one used with gaseous parents (2) has no direct equivalent here and a discussion about this parameter is useless for identifying a parent compound in the solid phase. As an example, measuring the scale length of the parent of formaldehyde, which is about 7000 km at 1 AU as mentioned in Sect. 1.1, is purely formal and unfortunately of no help in assessing the nature of the parent if it is in the solid phase.

2.2 Origin of H₂CO

Adjusting the spatial distribution of formaldehyde in Comet 1P/Halley would be quite simple considering the photodissociation of CH₃OH. If H₂CO is considered as the main CH₃OH photoproduct (for rate coefficients see Huebner et al. 1992), methanol would have to be produced from the nucleus at a level of 16% relative to water to obtain a good fit to measurements (Cottin et al. 2004). But methanol is only produced in amounts ranging from ~ 1 to 6% in comets (Bockelée-Morvan et al. 2004). Moreover, as discussed in Bockelée-Morvan et al. (1994), formaldehyde is not the main dissociation product of methanol, but rather the CH₃O methoxy radical. Thus, the additional source of cometary H₂CO is not consistent with a production from the CH₃OH photodissociation.

Formaldehyde is known to polymerize into long linear molecules $-(CH_2-O)_n-$ called polyoxymethylene (POM) (Fig. 4). This polymer was invoked in the cometary context to interpret a mass spectrum obtained with the PICCA instrument on board the Giotto spacecraft, between 8200 and 12600 km from the nucleus of Comet 1P/Halley. Indeed, Huebner (1987) suggested that the alternation of patterns with $\Delta m/z = 14$ and 16 shown in the PICCA spectrum is consistent with a sequence of $-CH_2-$ ($m = 14$) and $-O-$ ($m = 16$). But few years later, Mitchell et al. (1992) showed that the PICCA mass spectrum is not

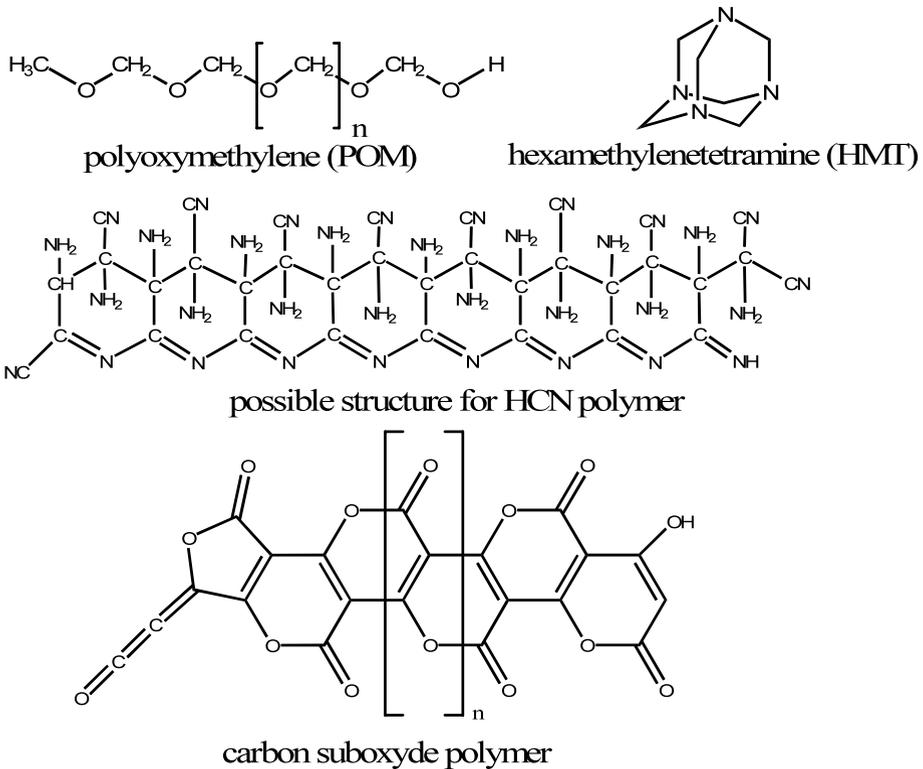


Fig. 4 Molecular structures of molecules evoked in this paper as possible parents for observed distributed sources. Structure of HCN polymer is one possible among others (see Minard et al. 1998 for more structures). Structure of carbon suboxide polymers proposed by Ballauff et al. (2004)

specifically characteristic of POM: the regular pattern observed is only the signature of a mixture of organic molecules composed of C, H, O, N atoms. Thus, even if the observed spectrum is not sufficient to establish its presence definitively, the presence of POM in cometary nucleus and dust particles cannot be ruled out at this stage. Furthermore, its production is possible under certain conditions in laboratory simulated interstellar and precometary ices (Schutte et al. 1993). Therefore, polyoxymethylene has often been suggested as the H_2CO distributed source (see, e.g. Boice et al. 1989, 1990; Meier et al. 1993; Eberhardt 1999). Boice et al. (1990) tried to estimate the production of formaldehyde from POM, but with the hypothesis that short polymer chains are emitted from dust particles and photodissociated in the gas phase. Because of the lack of experimental data, photodissociation rates were estimated from formaldehyde and related molecular bond strengths, without any direct laboratory measurement. Meier et al. (1993) showed that this does not fit the *Giotto* measurements.

First quantitative data considering the production of gaseous H_2CO by photo- and thermal-degradation of solid polyoxymethylene have been measured with the experimental setup shown Fig. 3 and described by Cottin et al. (2000) and Fray et al. (2004a). It has been shown that the major gaseous species produced by the photo-degradation of POM at 122 and 147 nm was H_2CO and CO and their production quantum yields have been measured (Cottin et al. 2000 and Table 2). Moreover, H_2CO is the sole gaseous species produced

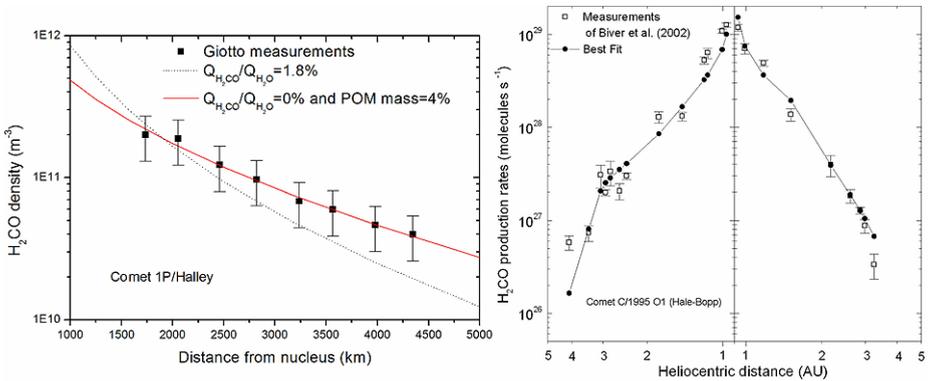


Fig. 5 On the left: H₂CO density profile in Comet 1P/Halley: measured by Giotto spacecraft (squares), and calculated considering a distributed source from solid polyoxymethylene (continuous line). This fit is obtained if POM represents 4% in mass of dust particles and H₂CO is not released from the nucleus. Dotted line is the best fit with no distributed source, obtained if 1.8% of H₂CO (relative to H₂O) is released from the nucleus. On the right: H₂CO production rates as a function of heliocentric distance in Comet C/1995 O1 (Hale-Bopp). The measurements of H₂CO are represented as open squares and the computed values as black circles. The latter have been obtained considering a POM mass fraction in the dust particles of 3.1% and H₂CO production at the surface of the nucleus equal to 3% of HCN production (i.e. $Q(\text{H}_2\text{CO})/Q(\text{H}_2\text{O}) = 0.0075\%$)

by the thermal-degradation of POM. Its production kinetics follows an Arrhenius law and the Arrhenius constants and activation energies have been measured (Fray et al. 2004a and Table 2).

The production of gaseous formaldehyde in the coma from solid polyoxymethylene has been modelled using these quantitative data. If we consider that a few percent in mass of POM is present on dust particles when they are ejected from the nucleus, the spatial distribution of H₂CO in 1P/Halley as well as the steep heliocentric evolution of the H₂CO production rates in Comet C/1995 O1 (Hale-Bopp) are quite well reproduced (Cottin et al. 2004; Fray et al. 2006) (Fig. 5).

The fact that POM can account for the distributed source of formaldehyde in two comets, within the same abundance range, and for observations as a function of the nucleus distance and also as a function of the heliocentric distance, strengthens the probability of its presence without being an actual detection of the polymer in comets. The presence of POM (or POM-like polymers) in the solid state on cometary dust particles is to date the best interpretation of observations.

2.3 Origin of CO

The case of the additional source for CO is more controversial than for H₂CO. As shown in Sect. 1.2, not all the observations are consistent. The photodissociation of several gaseous molecules (C₃O₂, H₂CO and CO₂) have been proposed to explain the origin of CO in the coma.

In Comet 1P/Halley, it has been proposed that gaseous carbon suboxide (C₃O₂) could be a precursor for CO by photodissociation (Huntress et al. 1991). If present in the atmosphere of comets, C₃O₂ would be photodissociated into CO and C₂O, C₂O being photodissociated into CO and C, and be a parent molecule at least for some CO (Crovisier 1994). Nevertheless, its upper limit in this comet (< 0.1%) is far from the amount required to produce the CO from secondary sources (7.5%) (Crovisier et al. 1991). Thus,

photodissociation of gaseous C_3O_2 cannot alone explain the formation of CO, even if it has been shown in the laboratory that it can be present in cometary ices (Brucato et al. 1997; Gerakines and Moore 2001). Looking for another gaseous parent, Meier et al. (1993) suggests that H_2CO is a precursor of 2/3 of the CO from an additional source, while later reanalysis of the data led to the conclusion that distributed formaldehyde produced from degradation of polyoxymethylene could fully explain all of the additional CO under certain assumptions such as the kinetics of POM degradation which were not known at that time (Eberhardt 1999). A comprehensive modelling with current knowledge of POM properties has yet to be done to settle this question for Comet 1P/Halley. If one considers CO_2 as a parent for CO, the CO Cameron system in the UV wavelength domain would be expected. It has been observed in several comets (Biermann 1976; Weaver et al. 1994; Bockelée-Morvan et al. 2004). This structure is thought to be produced mainly by prompt emission following the photodissociation of CO_2 . Therefore it is clear that the photodissociation of CO_2 also contributes to the CO production in the coma. Nevertheless, as the photodissociation rate of CO_2 is very low ($\beta_{CO_2} = 2 \cdot 10^{-6} \text{ s}^{-1}$) (Huebner et al. 1992), this mechanism cannot explain the observed scale length of the CO distributed source. In Comet 1P/Halley, it is not yet settled whether a mechanisms different than the photodissociation of other gaseous molecules has to be considered to explain the CO additional source.

In Comet C/1995 O1 (Hale-Bopp), the additional source of the CO in the atmosphere seems to be triggered at 2 AU (Disanti et al. 2001). The photolysis of a gaseous parent would not result in the same kind of observation, which suggests some thermal threshold from which a solid precursor might start to decompose and release CO in the gas phase. Looking for a solid precursor leads one to consider if POM could also be the origin of the additional CO. But even if photo-degradation of POM yields a small amount of CO (about the same order of magnitude than for H_2CO (Cottin et al. 2000), no CO is produced by thermal-degradation, which is the dominant degradation mechanism of POM for most of dust particles. Also, if CO from distributed sources in C/1995 O1 (Hale-Bopp) originated from POM degradation, then one should expect H_2CO production from distributed sources to at least equal that for CO, and more probably be larger by perhaps as much as one or two orders of magnitude. This would result in more H_2CO than CO in the coma, which is not the case. Thus, POM cannot be the main precursor for carbon monoxide.

As we already discussed in this section, gaseous carbon suboxide is not sufficient to produce the observed amount of CO from additional sources. But its polymer (carbon suboxide polymer, shown in Fig. 4) is known to decompose into CO_2 and CO when pyrolysed. The polymer starts to release some gas (CO_2) at about 400 K, but only due to structural changes, the mass loss is low. Above 500 K the polymer degrades with increased efficiency as the temperature rises and with an additional production of CO. The CO/ CO_2 ratio tends to 1/1 above 700 K and with increasing time (Blake and Hyde 1964; Smith et al. 1963). These studies show that if the same kind of polymers is present in comets, a distributed CO_2 source should also be observed, which, to date, is not the case. But laboratory synthesised polymer are extremely unstable as the compound is extremely hygroscopic (Schmedt auf der Günne et al. 2005). Exposed to air, it takes up atmospheric water within seconds and undergoes chemical modifications. Therefore, before reaching final conclusions about the relevance of this molecule in the cometary environment, new laboratory measurements have to be undertaken in controlled environment. Furthermore, no data about the photo-degradation of C_3O_2 polymers in VUV are currently available.

In Comet 29P/Schwassmann–Wachmann, located at large heliocentric distance, the temperature of the grains is so low that the distribution of CO in the coma can be explained by the slow sublimation of CO frozen on grains ejected from the nucleus (Gunnarsson et al. 2002, 2008). In this case, sublimation of the CO ice is a distributed source.

Because of the potential for multiple precursors, understanding the origin of CO from secondary and/or distributed sources requires probably a complete modelling work taking into account several gaseous and solid parents. Different compositions between comets, resulting in comets enriched or depleted in one or several precursors, and the use of different measurement methods probing different regions of the coma at different scales, could be an explanation for the contradictory observations.

2.4 Origin of HNC

In Comet C/1995 O1 (Hale-Bopp), Rodgers and Charnley (1998, 2005) and Irvine et al. (1998a, 1998b) show that the additional source for HNC could be accounted for by superthermal chemistry driven by fast hydrogen atoms ($\text{HCN} + \text{H}_f \rightarrow \text{HNC} + \text{H}$, with $\text{H}_f = \text{fast H}$). This would then be a secondary source. But this mechanism is only efficient in the relatively dense environment of Comet C/1995 O1 (Hale-Bopp), and due to the failure of such superthermal reactions to produce efficiently HNC in less active comets (Irvine et al. 2003; Rodgers and Charnley 2001, 2005), it seems more reasonable to look for other processes for the origin of HNC from additional sources.

Therefore, these authors propose the degradation of an unknown solid organic parent as the origin for the HNC from distributed sources. Candidates are the same as the ones presented and discussed in the next section for the parents of CN from distributed sources. However, quantitative and even qualitative data about its production by thermal or photo-degradation of refractory parents are rather difficult to obtain, since HNC is not easy to detect because of its rapid isomerisation into HCN in laboratory.

2.5 Origin of CN

The CN radicals may be produced by HCN photodissociation and another unknown mechanism. As the observed spatial distribution of CN is less distributed than the predicted distribution of CN produced solely by HCN photodissociation (Fig. 1), the scale length of the unknown production process has to be shorter than the observed production scale lengths (Fray et al. 2005). If the unknown mechanism is the photodissociation of a gaseous molecule, its lifetime has to be shorter than that of HCN. This is the case for HC_3N and C_2N_2 . Nevertheless, the HC_3N production rate measured in Comet C/1995 O1 (Hale-Bopp) does not seem to be sufficient to explain the CN distribution and C_2N_2 has never been detected in comets (Fray et al. 2005). Another hypothesis is a direct production of CN radical by degradation of complex refractory organic compounds present on cometary dust particles. This hypothesis has originally been proposed by A'Hearn et al. (1986) and Lamy and Perrin (1988). Hexamethylenetetramine (HMT) could be a candidate since it is easily synthesized from H_2CO and NH_3 during laboratory simulations of interstellar and precometary ices (Bernstein et al. 1995; Cottin et al. 2001; Muñoz Caro et al. 2004). But it has been shown that this compound is quite stable when photolyzed (Cottin et al. 2002) and no degradation has been observed when heated (HMT sublimates when heated) (Fray 2004). Thus HMT is surely not the parent molecule of CN. It has also been shown that HCN polymers, which have been proposed to be present in cometary nuclei (Rettig et al. 1992), produce HCN and NH_3 when heated (Fray et al. 2004b). Under certain circumstances, such polymers can be synthesized in interstellar or precometary ices (Gerakines et al. 2004). If one turns to other candidates, it must be noted that thermal-degradation of polyacrylonitrile leads to the formation of HCN, NH_3 and CH_4 (Xue et al. 1997) and that thermal-degradation of numerous synthetic nitrogen polymers also leads to

the formation of HCN (Michal 1982). As numerous nitrogenated compounds can produce HCN by thermal-degradation, more experiments have to be implemented to measure quantitative data needed for proper modelling.

Nevertheless, one should keep in mind that since CN parent scale length is shorter than the HCN photodissociation scale length (Fig. 1), CN has to be directly produced from the dust particles without HCN as an intermediary species (Fray et al. 2005). So far, all the experimental studies investigating the volatile compounds produced during photo- or thermal-degradation of nitrogenated organic matter have been performed in conditions in which CN radicals were not detectable, even if it was produced. Indeed, in laboratory conditions CN radicals are very reactive species turning very rapidly into HCN.

2.6 Origin of Sulfur Compounds

A recent analysis of SO interferometric observations in Comet C/1995 O1 (Hale-Bopp) concludes that the discrepancy between measured and computed values of the SO photodissociation rate may indicate that SO₂ is not the sole parent of SO, or that SO₂ is itself created by an additional source in the coma (Boissier et al. 2007). Whether this results from coma chemistry or a distributed source remains unknown.

Concerning NS detection in the same comet, Canaves et al. (2002, 2007), have published a detailed modelling of the chemistry of NS in cometary comae. Their most recent results conclude that the amount of detected NS in Comet C/1995 O1 (Hale-Bopp) can be explained by gas phase chemistry in the atmosphere. They call it a distributed source, but it would rather be a secondary source if we stick to the definitions proposed in the present paper.

Very limited interpretation can be given for distributed sources of sulfur bearing species. Indeed, except the recent references given hereabove, the literature lacks discussion about the origin of these species. If, much work remains to be done in the laboratory for C, H, O, N molecules, almost everything has to be done for C, H, S (and possibly O and N) molecules.

3 Conclusions

We are far from being able to understand the origin of distributed sources in comets. They are for sure a signature of complex chemistry in both gaseous and solid phases, but we still lack crucial data characterizing the physico-chemical properties of candidate parent compounds to reach final interpretations. More laboratory work is needed, mostly to measure how the complex refractory organic component of comets behaves on dust particles (photo- and thermal-degradation).

The discussions developed in the present paper should not leave the impression that all the distributed sources could be explained evoking the convenient degradation of some unknown solid material. If this process seems to be quite adapted to the case of formaldehyde, it is possible that it actually hides our current ignorance of some other chemical processes in the atmosphere of comets. Work remains before a conclusion can be formed. However, as our knowledge of the composition of the nucleus of comets derives from what we observe in their atmosphere, distributed sources are precious, though tangled, Ariadne's threads to follow.

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References

- M.F. A'Hearn, S. Hoban, P.V. Birch, C. Bowers, R. Martin, D.A. Klinglesmith, *Nature* **324**, 649–651 (1986). doi:[10.1038/324649a0](https://doi.org/10.1038/324649a0)
- M. Ballauff, S. Rosenfeldt, N. Dingenouts, J. Beck, P. Krieger-Beck, *Angew. Chem. Int. Ed.* **43**(43), 5843–5846 (2004). doi:[10.1002/anie.200460263](https://doi.org/10.1002/anie.200460263)
- M.P. Bernstein, S.A. Sandford, L.J. Allamandola, S. Chang, M.A. Scharberg, *Astrophys. J.* **454**, 327–344 (1995). doi:[10.1086/176485](https://doi.org/10.1086/176485)
- L. Biermann, NASA STI/Recon technical report N 77, 22023 (1976)
- N. Biver, D. Bockelée-Morvan, J. Crovisier, J.K. Davies, H.E. Matthews, J.E. Wink et al., *Astron. J.* **118**, 1850–1872 (1999). doi:[10.1086/301033](https://doi.org/10.1086/301033)
- N. Biver, D. Bockelée-Morvan, J. Crovisier, F. Henry, J.K. Davies, H.E. Matthews et al., *Astron. J.* **120**, 1554–1570 (2000). doi:[10.1086/301529](https://doi.org/10.1086/301529)
- N. Biver, D. Bockelée-Morvan, P. Colom, J. Crovisier, F. Henry, E. Lellouch et al., *Earth Moon Planets* **90**, 5–14 (2002a). doi:[10.1023/A:1021599915018](https://doi.org/10.1023/A:1021599915018)
- N. Biver, D. Bockelée-Morvan, J. Crovisier, P. Colom, F. Henry, R. Moreno et al., *Earth Moon Planets* **90**, 323–333 (2002b). doi:[10.1023/A:1021530316352](https://doi.org/10.1023/A:1021530316352)
- N. Biver, D. Bockelée-Morvan, J. Crovisier, D.C. Lis, R. Moreno, P. Colom et al., *Astron. Astrophys.* **449**, 1255–1270 (2006). doi:[10.1051/0004-6361:20053849](https://doi.org/10.1051/0004-6361:20053849)
- A.R. Blake, A.F. Hyde, *Trans. Faraday Soc.* **60**, 1775–1782 (1964). doi:[10.1039/tf9646001775](https://doi.org/10.1039/tf9646001775)
- D. Bockelée-Morvan, J. Crovisier, *Astron. Astrophys.* **151**, 90–100 (1985)
- D. Bockelée-Morvan, J. Crovisier, P. Colom, D. Despois, *Astron. Astrophys.* **287**(2), 647–665 (1994)
- D. Bockelée-Morvan, H. Rickman, *Earth Moon Planets* **79**, 55–77 (1997). doi:[10.1023/A:1006225030955](https://doi.org/10.1023/A:1006225030955)
- D. Bockelée-Morvan, J. Crovisier, *Earth Moon Planets* **89**, 53–71 (2000). doi:[10.1023/A:1021530016410](https://doi.org/10.1023/A:1021530016410)
- D. Bockelée-Morvan, D.C. Lis, J.E. Wink, D. Despois, J. Crovisier et al., *Astron. Astrophys.* **353**, 1101–1114 (2000)
- D. Bockelée-Morvan, J. Crovisier, M.J. Mumma, H.A. Weaver, in *Comets II*, ed. by M. Festou, H.U. Keller, H.A. Weaver (University of Arizona Press, Tucson, 2004), p. 391
- D. Bockelée-Morvan, N. Biver, E. Jehin, A.L. Cochran, H. Wiesemeyer, J. Manfroid et al., *Astrophys. J.* **679**, L49–L52 (2008). doi:[10.1086/588781](https://doi.org/10.1086/588781)
- D.C. Boice, D.W. Naegeli, W.F. Huebner, *Physics and mechanics of cometary materials*. ESA SP **302**, 83–88 (1989)
- D.C. Boice, W.F. Huebner, M.J. Sablik, I. Konno, *Geophys. Res. Lett.* **17**, 1813–1816 (1990). doi:[10.1029/GL017i011p01813](https://doi.org/10.1029/GL017i011p01813)
- J. Boissier, D. Bockelée-Morvan, N. Biver, J. Crovisier, D. Despois, B.G. Marsden et al., *Astron. Astrophys.* **475**, 1131–1144 (2007). doi:[10.1051/0004-6361:20078380](https://doi.org/10.1051/0004-6361:20078380)
- T.Y. Brooke, H.A. Weaver, G. Chin, D. Bockelée-Morvan, S.J. Kim, L.H. Xu, *Icarus* **166**, 167–187 (2003). doi:[10.1016/j.icarus.2003.08.008](https://doi.org/10.1016/j.icarus.2003.08.008)
- D. Brownlee, P. Tsou, Aléon et al., *Science* **314**, 1711–1716 (2006). doi:[10.1126/science.1135840](https://doi.org/10.1126/science.1135840) Medline
- J.R. Brucato, A.C. Castorina, M.E. Palumbo, M.A. Satorre, G. Strazzulla, *Planet. Space Sci.* **45**(7), 835–840 (1997). doi:[10.1016/S0032-0633\(97\)00071-8](https://doi.org/10.1016/S0032-0633(97)00071-8)
- M.V. Canaves, A.A. De Almeida, D.C. Boice, G.C. Sanzovo, *Earth Moon Planets* **90**, 335–347 (2002). doi:[10.1023/A:1021582300423](https://doi.org/10.1023/A:1021582300423)
- M.V. Canaves, A.A. de Almeida, D.C. Boice, G.C. Sanzovo, *Adv. Space Res.* **39**, 451–457 (2007). doi:[10.1016/j.asr.2006.09.040](https://doi.org/10.1016/j.asr.2006.09.040)
- L. Colangeli, J.R. Brucato, A. Bar-Nun, R.L. Hudson, M.H. Moore, in *Comets II*, ed. by M. Festou, H.U. Keller, H.A. Weaver (University of Arizona Press, Tucson, 2004), pp. 695–717
- P. Colom, J. Crovisier, D. Bockelée-Morvan, D. Despois, G. Paubert, *Astron. Astrophys.* **264**, 270–281 (1992)
- M.R. Combi, A.H. Delsemme, *Astrophys. J.* **237**, 633–640 (1980). doi:[10.1086/157909](https://doi.org/10.1086/157909)
- M.R. Combi, U. Fink, *Astrophys. J.* **484**, 879–890 (1997). doi:[10.1086/304349](https://doi.org/10.1086/304349)
- M.R. Combi, W.M. Harris, W.H. Smyth, in *Comets II*, ed. by M. Festou, H.U. Keller, H.A. Weaver (University of Arizona Press, Tucson, 2004), pp. 523–552
- H. Cottin, M.C. Gazeau, J.F. Doussin, F. Raulin, *Phys. Chem. Earth* **24**, 597–602 (1999)
- H. Cottin, M.-C. Gazeau, J.-F. Doussin, F. Raulin, *J. Photochem. Photobiol. Chem.* **135**(1), 53–64 (2000). doi:[10.1016/S1010-6030\(00\)00274-4](https://doi.org/10.1016/S1010-6030(00)00274-4)
- H. Cottin, C. Szopa, M.H. Moore, *Astrophys. J. Lett.* **561**(1), L139–L142 (2001). doi:[10.1086/324575](https://doi.org/10.1086/324575)
- H. Cottin, S. Bachir, F. Raulin, M.C. Gazeau, *Adv. Space Res.* **30**(6), 1481–1488 (2002). doi:[10.1016/S0273-1177\(02\)00508-2](https://doi.org/10.1016/S0273-1177(02)00508-2)
- H. Cottin, Y. Bénénilan, M.-C. Gazeau, F. Raulin, *Icarus* **167**, 397–416 (2004). doi:[10.1016/j.icarus.2003.10.009](https://doi.org/10.1016/j.icarus.2003.10.009)

- J. Crovisier, T. Encrenaz, M. Combes, *Nature* **353**, 610 (1991). doi:[10.1038/353610a0](https://doi.org/10.1038/353610a0) Medline
- J. Crovisier, *J. Geophys. Res.* **99**(E2), 3777–3781 (1994). doi:[10.1029/93JE02088](https://doi.org/10.1029/93JE02088)
- N. Dello Russo, M.A. Disanti, M.J. Mumma, K. Magee-Sauer, T.W. Rettig, *Icarus* **135**, 377–388 (1998). doi:[10.1006/icar.1998.5990](https://doi.org/10.1006/icar.1998.5990)
- D. Despois, H. Cottin, in *Lectures in Astrobiology*, ed. by M. Gargaud, B. Barbier, H. Martin, J. Reisse (Springer, Berlin, 2005), pp. 289–352
- M.A. Disanti, M.J. Mumma, N. dello Russo, K. Magee-Sauer, R. Novak, T.W. Rettig, *Nature* **399**, 662 (1999). doi:[10.1038/21378](https://doi.org/10.1038/21378) Medline
- M.A. Disanti, M.J. Mumma, N. Dello Russo, K. Magee-Sauer, *Icarus* **153**, 361–390 (2001). doi:[10.1006/icar.2001.6695](https://doi.org/10.1006/icar.2001.6695)
- M.A. DiSanti, M.J. Mumma, N. Dello Russo, K. Magee-Sauer, D.M. Griep, *J. Geophys. Res. Planets* **108f**, 15–11 (2003)
- P. Eberhardt, D. Krankowsky, Schulte et al., *Astron. Astrophys.* **187**, 481–484 (1987)
- P. Eberhardt, *Space Sci. Rev.* **90**(1/2), 45–52 (1999). doi:[10.1023/A:1005221309219](https://doi.org/10.1023/A:1005221309219)
- M.C. Festou, *Space Sci. Rev.* **90**, 53–67 (1999). doi:[10.1023/A:1005225426057](https://doi.org/10.1023/A:1005225426057)
- M.C. Festou, H.U. Keller, H.A. Weaver, *Comets II* (University of Arizona Press, Tucson, 2004)
- N. Fray, PhD thesis. Université Paris 12 (2004)
- N. Fray, Y. Bénilan, H. Cottin, M.-C. Gazeau, *J. Geophys. Res. Planets* **109**, E07S12 (2004a). doi:[10.1029/2003JE002191](https://doi.org/10.1029/2003JE002191)
- N. Fray, Y. Bénilan, H. Cottin, M.-C. Gazeau, R.D. Minard, F. Raulin, *Meteorit. Planet. Sci.* **39**, 4 (2004b)
- N. Fray, Y. Bénilan, H. Cottin, M.C. Gazeau, J. Crovisier, *Planet. Space Sci.* **53**, 1243–1262 (2005). doi:[10.1016/j.pss.2005.06.005](https://doi.org/10.1016/j.pss.2005.06.005)
- N. Fray, Y. Bénilan, N. Biver, D. Bockelée-Morvan, H. Cottin, J. Crovisier et al., *Icarus* **184**(1), 239–254 (2006). doi:[10.1016/j.icarus.2006.04.014](https://doi.org/10.1016/j.icarus.2006.04.014)
- P.A. Gerakines, M.H. Moore, *Icarus* **154**(2), 372–380 (2001). doi:[10.1006/icar.2001.6711](https://doi.org/10.1006/icar.2001.6711)
- P.A. Gerakines, M.H. Moore, R.L. Hudson, *Icarus* **170**, 202–213 (2004). doi:[10.1016/j.icarus.2004.02.005](https://doi.org/10.1016/j.icarus.2004.02.005)
- J.M. Greenberg, in *Comets*, ed. by L.L. Wilkening (University of Arizona Press, Tucson, 1982), pp. 131–163
- M. Gunnarsson, H. Rickman, M.C. Festou, A. Winnberg, G. Tancredi, *Icarus* **157**, 309–322 (2002). doi:[10.1006/icar.2002.6839](https://doi.org/10.1006/icar.2002.6839)
- M. Gunnarsson, D. Bockelée-Morvan, A. Winnberg et al., *Astron. Astrophys.* **402**, 383–393 (2003) doi:[10.1051/0004-6361:20030178](https://doi.org/10.1051/0004-6361:20030178)
- M. Gunnarsson, D. Bockelée-Morvan, N. Biver, J. Crovisier, H. Rickman, *Astron. Astrophys.* **484**, 537–546 (2008)
- L. Haser, *Bulletin de l'académie royale de Belgique* **43**, 740–750 (1957)
- J. Helbert, H. Rauer, D.C. Boice, W.F. Huebner, *Astron. Astrophys.* **442**, 1107–1120 (2005). doi:[10.1051/0004-6361:20041571](https://doi.org/10.1051/0004-6361:20041571)
- F. Henry, D. Bockelée-Morvan, J. Crovisier, J. Wink, *Earth Moon Planets* **90**, 57–60 (2002). doi:[10.1023/A:1021508216836](https://doi.org/10.1023/A:1021508216836)
- W.F. Huebner, *Science* **237**(August), 628–630 (1987). doi:[10.1126/science.237.4815.628](https://doi.org/10.1126/science.237.4815.628) Medline
- W.F. Huebner, J.J. Keady, S.P. Lyon, *Astrophys. Space Sci.* **195**, 1–294 (1992). doi:[10.1007/BF00644558](https://doi.org/10.1007/BF00644558)
- W.T. Huntress Jr., M. Allen, M. Delitsky, *Nature* **352**, 316–318 (1991). doi:[10.1038/352316a0](https://doi.org/10.1038/352316a0)
- D. Hutsemékers, J. Manfroid, E. Jehin, C. Arpigny, A. Cochran, R. Schulz et al., *Astron. Astrophys.* **440**, L21–L24 (2005). doi:[10.1051/0004-6361:200500160](https://doi.org/10.1051/0004-6361:200500160)
- W.H. Ip, in *Comets II*, ed. by M. Festou, H.U. Keller, H.A. Weaver (University of Arizona Press, Tucson, 2004), pp. 605–629
- W. Irvine, D. Bockelee-Morvan, Lis et al., *Nature* **382**, 418–420 (1996). doi:[10.1038/383418a0](https://doi.org/10.1038/383418a0)
- W.M. Irvine, E.A. Bergin, J.E. Dickens, D. Jewitt, A.J. Lovell, H.E. Matthews et al., *Nature* **393**, 547 (1998a). doi:[10.1038/311171](https://doi.org/10.1038/311171) Medline
- W.M. Irvine, J.E. Dickens, A.J. Lovell, F.P. Schloerb, M. Senay, E.A. Bergin et al., *Faraday Discuss.* **109**, 475–492 (1998b). doi:[10.1039/a709289j](https://doi.org/10.1039/a709289j) Medline
- W.M. Irvine, M. Senay, A.J. Lovell, H.E. Matthews, D. McGonagle, R. Meier, *Icarus* **143**(2), 412–414 (2000). doi:[10.1006/icar.1999.6281](https://doi.org/10.1006/icar.1999.6281) Medline
- W.M. Irvine, P. Bergman, T.B. Lowe, H. Matthews, D. McGonagle, A. Nummelin et al., *Orig. Life Evol. Biosph.* **33**, 609–619 (2003). doi:[10.1023/A:1025791101127](https://doi.org/10.1023/A:1025791101127) Medline
- W.M. Jackson, A. Scodinu, D. Xu, A.L. Cochran, *Astrophys. J.* **607**, L139–L141 (2004). doi:[10.1086/421995](https://doi.org/10.1086/421995)
- D.C. Jewitt, H.E. Matthews, T. Owen, R. Meier, *Science* **278**, 90–93 (1997). doi:[10.1126/science.278.5335.90](https://doi.org/10.1126/science.278.5335.90) Medline
- L.P. Keller, S. Bajt, G.A. Baratta et al., *Science* **314**, 1728–1731 (2006). doi:[10.1126/science.1135796](https://doi.org/10.1126/science.1135796) Medline
- J. Kissel, F.R. Krueger, J. Silén, B.C. Clark, *Science* **304**, 1774–1776 (2004). doi:[10.1126/science.1098836](https://doi.org/10.1126/science.1098836) Medline

- J. Kissel, F.R. Krueger, *Nature* **326**, 755–760 (1987). doi:[10.1038/326755a0](https://doi.org/10.1038/326755a0)
- P.L. Lamy, J.-M. Perrin, *Icarus* **76**, 100–109 (1988). doi:[10.1016/0019-1035\(88\)90142-X](https://doi.org/10.1016/0019-1035(88)90142-X)
- R. Meier, P. Eberhardt, D. Krankowsky, R.R. Hodges, *Astron. Astrophys.* **277**, 677–690 (1993)
- J. Michal, *Fire Mater.* **6**(1), 13–15 (1982). doi:[10.1002/fam.810060105](https://doi.org/10.1002/fam.810060105)
- S.N. Milam, A.J. Remijan, Womack et al., *Astrophys. J.* **649**, 1169–1177 (2006). doi:[10.1086/506501](https://doi.org/10.1086/506501)
- R.D. Minard, P.G. Hatcher, R.C. Gourley, C.N. Matthews, *Orig. Life Evol. Biosph.* **28**, 461–473 (1998). doi:[10.1023/A:1006566125815](https://doi.org/10.1023/A:1006566125815) Medline
- D.L. Mitchell, R.P. Lin, C.W. Carlson, A. Korth, H. Reme, D.A. Mendis, *Icarus* **98**, 125–133 (1992). doi:[10.1016/0019-1035\(92\)90213-Q](https://doi.org/10.1016/0019-1035(92)90213-Q)
- G.M. Muñoz Caro, U. Meierhenrich, W.A. Schutte, W.H.-P. Thiemann, J.M. Greenberg, *Astron. Astrophys.* **413**, 209–216 (2004). doi:[10.1051/0004-6361:20031447](https://doi.org/10.1051/0004-6361:20031447)
- T.W. Rettig, S.C. Tegler, D.J. Pasto, M.J. Mumma, *Astrophys. J.* **398**, 293–298 (1992). doi:[10.1086/171857](https://doi.org/10.1086/171857)
- S.D. Rodgers, S.B. Charnley, *Astrophysical J. Lett.* **501**(2), L227–L230 (1998). doi:[10.1086/311459](https://doi.org/10.1086/311459)
- S.D. Rodgers, S.B. Charnley, *Mon. Not. R. Astron. Soc.* **323**(1), 84–92 (2001). doi:[10.1046/j.1365-8711.2001.04099.x](https://doi.org/10.1046/j.1365-8711.2001.04099.x)
- S.D. Rodgers, S.B. Charnley, W.F. Huebner, D.C. Boice, in *Comets II*, ed. by M. Festou, H.U. Keller, H.A. Weaver (University of Arizona Press, Tucson, 2004), pp. 505–522
- S.D. Rodgers, S.B. Charnley, *Mon. Not. R. Astron. Soc.* **356**(4), 1542–1548 (2005). doi:[10.1111/j.1365-2966.2004.08606.x](https://doi.org/10.1111/j.1365-2966.2004.08606.x)
- S.A. Sandford, J. Aléon, C.M.O.D. Alexander et al., *Science* **314**, 1720 (2006)
- J. Schmedt auf der Günne, J. Beck, W. Hoffbauer, P. Krieger-Beck, *Chem. Eur. J.* **11**, 4429–4440 (2005). doi:[10.1002/chem.200401133](https://doi.org/10.1002/chem.200401133)
- W.A. Schutte, L.J. Allamandola, S.A. Sandford, *Icarus* **104**, 118–137 (1993). doi:[10.1006/icar.1993.1087](https://doi.org/10.1006/icar.1993.1087) Medline
- R.N. Smith, D.A. Young, E.N. Smith, C.C. Carter, *Inorg. Chem.* **2**(4), 829–838 (1963). doi:[10.1021/ic50008a041](https://doi.org/10.1021/ic50008a041)
- N. Thomas, D.C. Boice, W.F. Huebner, H.U. Keller, Intensity profiles of dust near extended sources on comet Halley. *Nature* **332**(6159), 51–52 (1988) doi:[10.1038/332051a0](https://doi.org/10.1038/332051a0)
- H.A. Weaver, P.D. Feldman, J.B. McPhate, M.F. A'Hearn, C. Arpigny, T.A. Smith, *Astrophys. J.* **422**, 374–380 (1994). doi:[10.1086/173732](https://doi.org/10.1086/173732)
- H.A. Weaver, T.Y. Brooke, G. Chin, S.J. Kim, D. Bockelée-Morvan, J.K. Davies, *Earth Moon Planets* **78**, 71–80 (1997). doi:[10.1023/A:1006227530238](https://doi.org/10.1023/A:1006227530238)
- J. Wink, D. Bockelée-Morvan, D. Despois, P. Colom, N. Biver, J. Crovisier et al., *Earth Moon Planets* **78**, 63–63 (1997). doi:[10.1023/A:1006263026604](https://doi.org/10.1023/A:1006263026604)
- M. Womack, M.C. Festou, S.A. Stern, *Astron. J.* **114**, 2789–2796 (1997). doi:[10.1086/118687](https://doi.org/10.1086/118687)
- T.J. Xue, M.A. McKinney, C.A. Wilkie, *Polym. Degrad. Stabil.* **58**(1–2), 193–202 (1997). doi:[10.1016/S0141-3910\(97\)00048-7](https://doi.org/10.1016/S0141-3910(97)00048-7)
- L.M. Ziurys, C. Savage, M.A. Brewster, A.J. Apponi, T.C. Pesch, Wyckoff, *Astrophys. J. Lett.* **527**(1), L67–L71 (1999). doi:[10.1086/312388](https://doi.org/10.1086/312388)