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# The formation and composition of the atmospheres of small solar system bodies

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## Abstract

This review will concentrate on recent developments and on ill-known or controversial topics concerning the formation and composition of atmospheres around small solar system bodies :
- What reliable informations do we have on the chemical abundances of these atmospheres ? Obviously, all the constituents have not yet been identified.
- How do these gas-phase abundances reflect the composition of the nucleus and the history of its formation ? The gas composition is expected to be strongly affected by sublimation fractionation.
- What is the role of grains in the release of volatiles ? Grains are commonly invoked for the origin of an extended source of CO, but no convincing mechanism for the release of CO has yet been proposed.
- What are the volatiles responsible for cometary activity ? Renewed interest in this topic comes from the discovery of cometary activity at large heliocentric distances.
- How gas jets are formed and how do they evolve ? Why does the gas coma look so symmetric ?
- What are the relations between comets and asteroids ? Are there many objects belonging to both classes.

We will show how future ground-based and space-borne observations, as well as laboratory investigations, could help resolving these problems.

## Introduction

Primitive volatile molecules are trapped in cometary nuclei. When these bodies are entering the inner Solar System, these volatiles are released to form transient atmospheres around the solid nuclei. We will review here recent developments on this subject: (i) new insights on the composition of cometary atmopheres and their relation to the composition of cometary nuclei; (ii) the possibility of outgassing from cometary grains; (iii) the discovery of transient atmospheres around asteroids and distant comets.

## The composition of cometary atmospheres

Since 1985, a quantum leap forward has been taken in our knowledge of the gas composition of cometary atmospheres. Before that date, the study of cometary composition was mostly based on observations in the visible and ultraviolet which essentially revealed decomposition products of directly sublimed volatiles, with the exception of CO and $S_2$. The direct identification of parent molecules became tractable with a theoretical understanding of their excitation conditions, which showed that these molecules should be searched for in the infrared and radio range, and the development of suitable and sensitive instrumentation for observing them. At the present time, eight parent volatiles have been unambiguously detected by remote sensing observations. In addition, significant abundance upper limits were obtained. Indirect studies and in situ measurements by the various spacecraft that encountered P/Halley also provided interesting informations regarding key molecules for cometary formation. A summary of parent molecular abundances with respect to water and a selection of upper limits are given in Table 1. We will briefly comment on this table, with an emphasis on some molecules for which controversial results have been published. Further discussions on this subject can been found in Krankowsky 1991 and Mumma et al. 1992.

Table 1: Abundances of parent molecules observed in comets.

| Species | Abundance | Comet a) | Observation |
|---|---|---|---|
| *direct determinations :* | | | |
| $H_2O$ | 100 | P/Halley, Wilson | IR |
| CO | 2 - 20 b) | West, P/Halley ... | UV |
| $CO_2$ | 3 | P/Halley | IR |
| $H_2CO$ | 0.03 - 4 b) | P/Halley, P/B-M, Austin, Levy | radio, IR |
| $CH_3OH$ | 1 - 4 | Austin, Levy | radio, IR |
| HCN | 0.05 - 0.2 | P/Halley, P/B-M, Austin, Levy ... | radio |
| $H_2S$ | 0.2 | Austin, Levy | radio |
| $S_2$ | 0.05 | IRAS-A-A | UV |
| *indirect determinations :* | | | |
| $NH_3$ | 0.1 - 0.2 | P/Halley ... | (c) |
| $N_2$ | 0.02 | P/Halley | (d) |
| *selected upper limits :* | | | |
| HCOOH | < 0.2 | Levy | radio |
| $C_2H_5OH$ | < 0.5 | Levy | radio |
| $HC_3N$ | < 0.01 | Levy | radio |
| OCS | < 0.2 | P/Halley, Levy | radio, IR |
| $SO_2$ | < 0.001 | Bradfield, P/Halley | UV |

a) West (1976 VI), Bradfield (1979 X), IRAS-Araki-Alcock (1983 VII), P/Halley (1986 III), Wilson (1987 VII), P/Brorsen-Metcalf (1989 X), Austin (1990 V), Levy (1990 XX)

b) Variable from comet to comet. It is not known to which extend this species is parent or daughter.

c) Indirectly inferred from observations of the NH and $NH_2$ radicals in the visible.

d) Indirectly inferred from observations of the $N_2^+$ ion in the visible.

### *Water*

Water was directly identified for the first time in a comet in December 1985, 35 years after the publication of the model of the "dirty snow ball" of Whipple (1950). 10 lines of the $\nu_3$ band at 2.7 µm were detected in P/Halley using the Kuiper Airbone Observatory (Mumma et al. 1986). The $\nu_3$ band of water was later detected in IKS spectra acquired on the Vega-1 experiment (Combes et al. 1988). The KAO observation was repeated in the dynamically new comet Wilson (1987 VII) (Larson et al. 1989). Absolute production rates, when compared with those of other species, confirmed that water is indeed the dominant volatile species of cometary nuclei, with ~ 80 % by number (Krankowsky et al. 1986).

### *Carbon monoxide and carbon dioxide*

Carbon monoxide CO was first detected in the UV in comet West (1976 VI), through rocket ultraviolet observations in the range 140-180 nm (Feldman & Brune 1976). It was subsequently searched for in many comets with the International Ultraviolet Explorer (IUE) or sounding rockets. It was detected in only a few comets, with highly different abundances with respect to water: from 2% in comet Bradfield (1979 X) to 15-20 % in comets West (1976 VI) and P/Halley (Feldman 1983; Woods et al. 1986). The radial density distribution of CO observed in P/Halley with the Giotto Neutral Mass spectrometer suggests the presence of an extended source contributing to half of the total production of CO (Eberhardt et al. 1987). CO was marginally detected by the IKS-Vega spectrometer through its vibrational band v = 1-0 at 4.7 µm (Combes et al. 1988). A possible detection of the P(3) rovibrational line of the CO 4.7 µm band was recently reported by DiSanti et al. (1992) for comet Austin (1990 V), but the non-detection of the P(2) line made this detection of CO only tentative.

Carbon dioxide is also an important contributor to the carbon inventory in cometary volatiles with an abundance relative to water of 3.5 %. It was only detected in IKS-VEGA spectra of P/Halley, through its vibrational band at 4.3 µm (Combes et al. 1988). Unfortunately $CO_2$ is not observable directly from the ground due to telluric absorption of its strong infrared bands and to the absence of rotational lines.

### *Formaldehyde*

The detection of formaldehyde was claimed at several occasions: at radio wavelengths from its rotational transitions at 6 cm (Snyder et al. 1989), 225 GHz (Colom et al. 1992) and 352 GHz (Schloerb & Ge 1992), in the infrared from its vibrational band at 3.56 µm (Combes et al. 1988; Mumma & Reuter 1989), in the visible (e.g. Valk et al. 1992) and from the in situ measurements of the neutral and ions mass spectrometers aboard Giotto (Krankowsky 1991; Meier et al. 1991; Geiss et al. 1991). Abundance mixing ratios up to 4 % percent were derived in P/Halley from the centimetre and infrared observations and the in situ measurements. In contrast, formaldehyde abundances between 0.03 % and 0.5 % only were inferred from the millimetre lines detected in comets P/Brorsen-Metcalf (1989 X), Austin

(1990 V) and Levy (1990 XX), in the assumption of direct release from the nucleus. These small abundances are consistent with upper limits derived from infrared observations of the same comets (Reuter et al. 1992). It is not yet clear, however, that this large diversity observed from comet to comet and along the trajectory of P/Halley reflects real differences or heterogeneities in the formaldehyde content of cometary nuclei. Indeed, as discussed by Bockelée-Morvan & Crovisier (1992), the detections of formaldehyde in P/Halley are marginal or ambiguous. Furthermore, part of the observed formaldehyde may originate from an extended source, as suggested by the in situ measurement and not excluded by the millimetre and submillimetre data: this has to be properly taken into account in the abundance retrievals.

### *Methanol*

Methanol was first identified in comet Austin (1990 V) through several of its rotational lines at 145 GHz (Bockelée-Morvan et al. 1991, 1992) and its vibrational band at 3.52 µm (Hoban et al. 1991). $CH_3OH$ was later detected in comet Levy (1990 XX) from a dozen of its rotational lines (Bockelée-Morvan et al. 1990, 1992). These observations show that methanol is a significant constituant of cometary atmospheres with abundances of 4% and 1% in comets Austin and Levy, respectively. A similar amount of methanol was recently derived for comet Halley from the analysis of ion and neutral mass spectra (Geiss et al. 1991; Eberhardt et al. 1991) and from the study of infrared spectra covering the 3.52 µm methanol band (Reuter 1992).

### *Methane*

The case for methane deserves a particular attention since this species is, together with CO, $NH_3$ and $N_2$, a key molecule for testing chemical models of the solar nebula and dense interstellar clouds where cometary ices might have condensed (Lewis & Prinn 1980; Prasad & Huntress 1980). Ground-based infrared spectroscopy of the rovibrational lines of the $\nu_3$ band of $CH_4$ around 3.3 µm has led to sensitive 3-$\sigma$ abundance upper limits in the range of 0.2 - 1.2 % in comet P/Halley (Kawara et al. 1988), 1.4 - 4.5 % in comet Wilson (1987 VII) (Larson et al. 1989) and 0.3 - 2 % in comet Levy (1990 XX) (Brooke et al. 1991). Larson et al. report a possible detection in comet Wilson that exceeds the 3-$\sigma$ noise level, but too marginal to constitute a definite spectroscopic identification of $CH_4$. From Giotto ion mass spectrometer data, Allen et al. (1987) deduced an abundance of methane of 2 % in comet Halley. Their analysis is based on the interpretation of the 15 amu/e peak as mainly due to $CH_3^+$ and on the assumption that methane is the prevailing source for this ion. Since the contributions of methanol and other organic compounds containing the methyl group have been neglected, this methane abundance may have been overestimated. Allen et al. (1987) furthermore pointed out that cumulative uncertainties in the data and in the input parameters of their chemical model may increase or decrease their inferred $CH_4$ abundance by a factor of 4.

## *Nitrogen compounds*

Only one nitrogen parent volatile, HCN, has been directly identified by molecular spectroscopy. Detection of this molecule was claimed for the first time in comet Kohoutek (1972 XIII) through its J(1-0) rotational line at 89 GHz (Huebner et al. 1974). HCN was subsequently detected in other comets, at various millimetre or submillimetre wavelengths (Crovisier & Schloerb 1991; Bockelée-Morvan et al. 1990; Schloerb & Ge 1992; Winnberg 1990). The HCN abundance relative to water varies from 0.05 % to 0.2 % depending on the comet. The value inferred in comet Halley (0.1 - 0.2 %) agrees with that derived from the 28 amu/e peak in the ion spectra obtained by the Giotto IMS experiment, interpreted as being mainly due to protonated hydrogen cyanide (Geiss et al. 1991). Searches for other nitrogen compounds ($CH_3CN$, $HC_3N$, $HC_5N$ ...) in the millimetre range resulted in upper limits only, which are on the order of 0.1 % or less (Bockelée-Morvan et al. 1987; Crovisier et al. 1992).

The direct detection of ammonia at radio wavelength in comet IRAS-Araki-Alcock (1983 VII) (Altenhoff et al. 1983) was never confirmed in subsequent comets. The interpretation of spectra of $NH_2$ and NH in the visible in terms of $NH_3$ as a parent of both leads to an ammonia abundance of 0.1 - 0.2 % depending on the comet (Wyckoff et al. 1991). This value is by a factor of ten lower than that derived from the analysis of the ratio $NH_4^+/H_3O^+$ measured by the 18 and 19 amu/e peaks in Giotto Ion Mass Spectrometer data (Allen et al. 1987). However, Geiss et al. (1991) pointed out that reactions of $H_3O^+$ with molecules heavier than $H_2O$ and high proton affinity were neglected, leading to an overestimation of $H_3O^+$ reacting with $NH_3$ to give $NH_4^+$, and an overestimation of $NH_3/H_2O$.

Molecular nitrogen $N_2$ is presently not detectable in comets with spectroscopy, having no allowed vibrational or rotational transitions and no electronic transition in the accessible UV range. Abundance upper limits of 10 % and 1.5 % were derived from Giotto Neutral and Ion mass spectrometers, respectively (Eberhardt et al. 1987; Balsiger et al. 1986). The abundance of $N_2$ was estimated to 0.02 % from the analysis of the $N_2^+/CO^+$ abundance ratio measured in the visible in the tail of P/Halley (Wyckoff et al. 1991).

## *Sulfur compounds*

Two sulfur-bearing parent volatiles were directly identified by molecular spectroscopy. $S_2$ was only detected in comet IRAS-Araki-Alcock (1983 VII) at ultraviolet wavelengths with a relative abundance of 5 $10^{-4}$ (A'Hearn et al. 1983; Budzien & Feldman 1992). More recently, hydrogen sulfide $H_2S$ was identified at millimetre wavelengths in comets Austin (1990 V) and Levy (1990 XX) at an abundance level of 0.2 % relative to water (Crovisier et al. 1991). The analysis of ions mass spectra obtained by the PICCA and IMS instruments on board Giotto yielded $H_2S$ abundances in comet P/Halley between 0.1 % and 0.4 % (Marconi et al. 1990, reanalyzed by Crovisier et al. 1991; Geiss et al. 1991). The $CS_2$ molecule, which is the prime candidate for the production of the CS radical observed in many comets with IUE, is likely present at the 0.1 % level (Feldman 1991). The abundance of sulfur coming from $H_2S$, $CS_2$ and $S_2$ is smaller than the abundance of atomic sulfur of 2 % observed in the atmosphere (Azoulay & Festou 1986), suggesting that sulfur parent molecules are missing. Searches for other sulfur compounds in the UV (SO, $SO_2$: Kim and A'Hearn 1991), the millimetre range (OCS, $H_2CS$, $SO_2$: Crovisier et al. 1991) and the infrared range (OCS: Combes et al. 1988; DiSanti et al. 1992) were negative and placed sensitive upper limits on their abundances.

### *Reliability of abundance determinations*

The determinations of cometary molecular abundances or their upper limits from remote-sensing spectroscopic observations are more or less uncertain since they rely upon models and various input parameters. Errors may be as large as a factor of two or even more for some of them, and it may be useful to recall the sources of uncertainties proper to observations of electronic, vibrational and rotational transitions, and those common to all observations.

The first step in the derivation of molecular abundances, after calibration of the observations, is the conversion of line intensities into molecular column densities. It involves modelling of the excitation and emission processes. Possible sources of errors in the interpretation of electronic bands, whose emissions result from resonant fluorescence pumped by solar radiation, are: 1) uncertainties in the branching ratio between dissociation and radiative decay (e.g. SO, Kim & A'Hearn 1991; $H_2CO$, Bockelée-Morvan & Crovisier 1992); 2) lack of accurate solar spectrum which depends on solar activity in the far UV and is highly denticulate in the near UV and visible causing the Swings effect; 3) imperfect fluorescence calculations: cf $S_2$ whose abundance has been reevaluated by a factor of 2 using time dependent calculations (Kim et al. 1991) or the upper limit obtained for $SO_2$ which is affected by the lack of spectroscopic data (Kim & A'Hearn 1991). Uncertainties related to the modelling of the total fluorescence emission of vibrational bands of parent molecules are generally small provided total band strengths are accurately measured in the laboratory (this is not yet the case for the $\nu_3$ band of $CH_3OH$ at 3.52 μm, which is blended with the $\nu_2$ and $\nu_9$ bands at room temperature; Hoban et al. 1991). Uncertainties in the interpretation of individual ro-vibrational lines are much larger since an accurate knowledge of the population distribution of the rotational levels is required (e.g. abundance upper limits inferred for $CH_4$ were found to vary by a factor of 6 within rotational temperatures of 50-200 K). A complete treatment of the overall rotational excitation of the molecule is particulary needed for interpreting rotational lines observed in the radio or submillimetre range. For such modelling one need to know the gas kinetic temperature, and possibly that of electrons, collisional cross-sections with the main partner and vibrational band strengths, in order to take into account collisional and radiative IR excitation. Errors may be particularly large when the collisional region is sampled due to the ill-known kinetic temperature (line intensities scale as $T^{-3/2}$ for asymmetric top molecules). These uncertainties, however, can be constrained by observing several rotational lines (e.g. $H_2S$, Crovisier et al. 1991; $CH_3OH$, Bockelée-Morvan et al. 1992). Errors can be also introduced in modelling radiative transfer, when required (e.g. HCN at 269 GHz).

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The second step is the conversion of column densities into production rates, for which one needs the molecular space distributions. The photodissociation rates are presently calculated from laboratory absorption spectra at room temperature and may not be quite appropriate for the much lower coma temperatures. Laboratory data are furthermore not always available. A Haser description of the density is always used, while isotropy and steady state do not generally apply. But the main source of errors is in the assumption generally made that stable molecules come from the nucleus while some of them might be produced by a distributed source (e.g. CO and $H_2CO$, as discussed above).

Finally, in order to compare molecular abundances from comet to comet, production rates are generally scaled relative to water. Since cometary activity is known to be variable, additional uncertainties may be introduced when simultaneous observations of a tracer of $H_2O$ like OH are not available.

## From the coma composition to the nucleus composition

From production rates measured in the atmosphere, several molecular (like $CO/CH_4$) or elemental (like C/O) abundance ratios have been the object of qualitative and quantitative discussions in terms of cometary formation. One can wonder, however, to which extent the gas-phase abundance ratios do reflect the initial composition of the nuclei. This question has received a larger attention this last decade, with the development of experimental studies on the thermodynamical properties of water ice and ice mixtures and theoritical simulations of the thermal behavior of cometary nuclei entering the inner solar system. It seems now clear that volatiles did not originally condense in the form of clathrate hydrates controlling the evaporation of all species, as formerly suggested by Delsemme & Swings (1952) in order to explain the simultaneous outgassing of species of different volatility, but in the form of amorphous icy grains in a very porous structure. As explained by Schmitt & Klinger (1987), the species with relatively low volatility, which can be efficiently trapped in the amorphous $H_2O$-ice matrix, either in the build up of pre-cometary ices or in subsequent warming, should be released only during water ice evaporation and their production rate relative to water should be representative of their mixing ratio in the nucleus. On the other hand, the abundances of the species of high or moderate volatily observed in the coma are expected to be a complex function of the initial composition of the comet and of the physical and thermal history of the internal parts of the nucleus (Espinasse et al. 1991). Indeed, both the inner layers of the nucleus, diffusing towards the surface, and the outer layers, progressively depleted in volatiles, contribute to the gas production. In addition, the diffusion and recondensation inwards the nucleus may enrich the deepest regions, while crystallization of amorphous ice produces an onset of release of volatiles. This could explain the large variability, with time and from comet to comet, observed for the abundances of the volatile species CO, $CO_2$ (traced by $CO_2^+$) and possibly $H_2CO$, while the parent species of CN (HCN), $C_2$ and $C_3$, likely less volatile, exhibit more constant production rates relative to water. Due to the relatively low volatility of methanol, it is likely that the differences observed between comets in the $CH_3OH$ abundances reflect diversity in the composition of the nuclei. The case for $H_2S$, for which a similarity between two comets has been observed, is less clear since this molecule condenses at temperatures intermediate between those of CO and $CO_2$. Further laboratory experiments on the physical properties of ice mixtures are needed to clarify the relation between coma and nuclei mixing ratios.

## Outgassing from dust

### *Evidences for outgassing from grains*

The idea that part of the cometary gas-phase molecules and radicals could come from grains is suggested by several evidences, most of them first observed in P/Halley:

- The existence of CN jets in spectral images of P/Halley (A'Hearn et al. 1986); the existence of $C_2$ jets is also possible.
- The CO distribution observed in P/Halley: the total CO production rate is about 20% relative to water. The production of CO from the nucleus is only 5%. The remaining CO is presumed to come from a distributed source with a scalelength of the order of $10^4$ km (Krankowsky 1991). Decomposition of known cometary CO-bearing molecules ($CO_2$, $H_2CO$, $CH_3OH$) can not explain the abundance and/or the scalelength of the distributed CO.
- It is also possible that $H_2CO$ comes from a distributed source (see the discussion in Snyder et al. 1989 and Colom et al. 1992).
- The mass spectroscopy investigations of P/Halley from VEGA and Giotto (Jessberger & Kissel 1991) revealed that an important fraction of the grains is composed of CHON elements.

It must be noted that alternative explanations can be given to all of these arguments. For CN jets, Combi (1987) suggested that a non-homogeneous composition of the active regions would result in non-homogeneous jets which are preserved during coma expansion. The space distribution of CO observed in situ in P/Halley could be due to the crossing of a jet by the spacecraft. The decomposition of yet unidentified CHO species directly sublimed from the nucleus could be a significant source of CO. Finally, the existence of CHON grains does not mean that they can easily relase organic molecules or radical (see below).

### *Icy grains*

The existence of icy grains as a major constituent of cometary comae has been postulated for a long time (Delsemme & Miller 1971). The *Icy Grain Halo* was invoked as a possible explanation to the unexpectedly large radio continuum occasionally observed in comets (Gibson & Hobbs 1981). However, these large radio fluxes were not confirmed by recent observations (reviewed by Crovisier & Schloerb 1991). Several attempts to detect the infrared signature of ice around 2.9 µm gave inconclusive results (reviewed by Tokunaga & Brooke 1990). On the other hand, the presence of stable icy grains in comae developped at large heliocentric distances, such as those resulting from the outbursts of Chiron and P/Halley, is very probable. Their contribution to outgassing for intermediate heliocentric distances may be significant, and they were invoked by A'Hearn et al. (1984) to explain the observations of comet Bowell 1982 I at 3 AU.

Icy grains, except for very large sizes or in the very unlikely case of pure-ice grains, have very short life times at heliocentric distances ~ 1 AU or smaller (Lichtenegger & Kömle 1991). The release of volatiles from cometary grains is thus very rapid and should happen in the first few kilometres from the nucleus; therefore, ground-based observers could not distinguish between volatiles from the nucleus and volatiles from grains.

As an example, the sublimation and photodissociation of carbon suboxide ($C_3O_2$) from grains was invoked to explain the observed distributed source of CO (Huntress et al. 1991). However, $C_3O_2$ is a highly volatile species, more volatile than water, and could not remained trapped in grains for a significant time. A very stringent upper limit (< 0.001 relative to water) to the release of $C_3O_2$ from the circumnuclear region was set up by Crovisier et al. (1991) from the IKS/VEGA observations of P/Halley.

The existence of icy grains could be fraught with consequences for the coma hydrodynamics. If a significant portion of the coma gas is coming from icy grains, even close to the nucleus, the gas kinematics may be completely changed. The collisional region may be smaller by orders of magnitudes; the gas temperature and expansion velocity may be completely different. This might suggest a test to the existence of icy grains. The process of recondensation-sublimation of water from the nucleus may also be important (Crifo 1992).

Table 2: Volatility of possible cometary constituents.

| | | | |
|---|---|---|---|
| Highly volatile | < 80 K | $N_2$, CO, $CH_4$, $CO_2$ | responsible for distant activity |
| "Intermediate" | 60-120 K | $H_2S$, $H_2CO$, $NH_3$, HCN, $CH_3OH$ | strongly polar, sublimation linked to that of water |
| Volatile | 150-200 K | $H_2O$ | activity at $r_h < 3$ AU |
| Semi-refractory | 200-400 K | POM, $S_2$, small PAH's | sublimation from grains and inactive nucleus |
| Refractory | > 400 K | kerogen, polymers, minerals | only released in Sun-grazing comets |

### *Refractory and semi-refractory organics on grains*

CHON grains were observed at distances a few $10^3$ to a few $10^4$ km from P/Halley's nucleus. As discussed above, volatile organics would have already sublimed at these distances. Thus we surmise that the CHON grains are composed of refractory or semi-refractory organics such as large molecules and polymers. Table 2 presents a synopsis of the volatility of possible cometary materials.

PAH's (Polycyclic Aromatic Hydrocarbons) ay significantly sublimate in the environment of comets at $r_h$ = 1 AU: benzene is as volatile as water; small PAH's such as anthracene or phenanthrene have equilibrium sublimation temperatures of about 200 K. The presence of aromatics in comae is suggested from their characteristic band at 3.28 µm (Encrenaz & Knacke 1991); are they in the gas phase, or stuck at the surface of grains ? Polyoxymethylene $(H_2CO)_n$ apparently may be easily thermally relased from grains (Möller & Jackson 1990). Its dissociation products might explain the presence of many of the peaks of the mass spectra (Huebner et al. 1987) and perhaps the distributed source of $H_2CO$ or even CO. However, to our knowledge, no quantitative analysis of the photodestruction of this species has yet been made.

There is at least one example of the release of a semi-refractory species: the $S_2$ molecule observed in comet IRAS-Araki-Alcock (A'Hearn et al. 1983). However, the observed distribution of $S_2$ shows that it is released from the nucleus or very close to the nucleus.

The release of radicals and refractories from grains requires higher-energy processes. Radical sputtering following impact of solar-wind particles or hot ions is possible, but this process fails by orders of magnitudes to produce the observed abundances of radicals (Moore & Tanabé 1990). Molecules in the solid phase generally cannot be broken as easily as small gas-phase molecules by solar UV. A recent KOSI experiment simulated VUV exposition of cometary materials (Roessler et al. 1992). The photon fluence corresponded to about 40 days of solar irradiation at 1 AU; thus, the results can not really inform us on the photosputterring of grains in the inner coma which receive a much smaller amount of radiation (most of the grains stay less than one day at $r < 10^4$ km). An important result is that minerals and kerogen are relatively resistant to VUV photolysis. The HCN polymers investigated in that experiment do not yield CN radicals: adenine $(HCN)_5$ is stable; triazine $(HCN)_3$ sublimates and dissociates into HCN.

Thus, there is not yet any experimental basis to explain the direct production of CN radicals from grains. CN emission was possibly observed from Chiron at 11 AU from the Sun (Bus et al. 1991). HCN is an identified CN-parent which is indeed more volatile (95 K) than water (152 K), but not as much as CO (24 K). At 11 AU, the equilibrium temperature of grains and surfaces is about 85 K, which is barely enough for an efficient release of HCN. This suggests a source for CN other than HCN. It must be noted that it is much more difficult to photosputter CN from the cold CHON grains of Chiron, with a UV flux 100 times smaller than at 1 AU.

We conclude that if volatiles are released from cometary grains, their release is very rapid and happens close to the nucleus. Refractories are just refractories and cannot be stripped from the grains or be destructed, except by high-energy processes, which have very low rates. There is still place, however, for sublimation of *semi-refractories* from heated dust grains (or from the hot *inactive* surface of the nucleus).

## Relations between comets and asteroids

This topic has been discussed many times in the past and we will only concentrate on recent developments. It is beyond the scope of the present paper to discuss the dynamical evolution of comets and asteroids and their possible relations.

*From asteroids to comets.*

There are many examples of small bodies first designated as asteroids which had later to be reclassified as comets. Recent cases are P/Parker-Hartley 1987 XXXVI = 1986 TF (IAU Circ. 4752) and P/Shoemaker-Levy 2 1990 VI = 1990 UL3 (IAU Circ. 5149), but the most famous example is undoubtedly 2060 Chiron (French et al. 1989). Chiron has an unusual orbit for an asteroid and was for some time the most distant known asteroid. Its diameter is evaluated to about 200 km, but it might be as large as 400 km (Syke & Walker 1991). From photometric monitoring, a brightening excess was observed, revealing activity. Then, a coma was definitly detected (Luu & Jewitt 1990; Meech & Belton 1990). The CN band was possibly detected (Bus et al. 1991). Note that Chiron has not been renamed as a comet.

Chiron is probably not unique. Two objects of large sizes (of the order of 100 km in diameter) were recently discovered in the outer solar system: 1991 DA (*IAU Circ.* 5208) with an Halley-type orbit and (5145) 1992 AD (*IAU Circ.* 5434, 5450, 5480) with a Chiron-type orbit and an exceptional red color (Hoffmann et al. 1992). No definite sign of activity has been detected up to now in these objects.

There are also cases of more "conventional" asteroids for which activity is suspected (Table 3). Photometric observations of 2201 Oljato suggest molecular fluorescent emission (McFadden 1990). Yeomans (1991) has pointed out the cases for 1862 Apollo and 1566 Icarus, two Earth-crossing asteroids, whose orbits might be affected by non-gravitational forces, and which therefore might undergo cometary activity (the gas production rate of 1862 Apollo should be of the order of $10^{26}$ $s^{-1}$ to account for the non-gravitational forces). In Ceres, the detection of OH ultraviolet emission was recently claimed by A'Hearn & Feldman (1992).

Table 3: Asteroids with possible cometary activity.

| name | semi-axis AU | excentricity | diameter km | remark |
|---|---|---|---|---|
| 2060 Chiron | 13.75 | 0.38 | ~200 | cometary activity |
| 1991 DA | 11.88 | 0.87 | ~100 | no activity |
| (5145) 1992 AD | 20.48 | 0.58 | ~100 | no activity |
| 2201 Oljato | 2.17 | 0.71 | 1.4 | fluorescence ? |
| 1862 Apollo | 1.47 | 0.56 | 1.5 | NGF ? |
| 1566 Icarus | 1.08 | 0.83 | 0.9 | NGF ? |
| 1 Ceres | 2.77 | 0.10 | 913 | OH emission ? |

Several systematic searches for cometary activity in near-Earth asteroids were undertaken: spectroscopic searches for molecular signatures (Cochran et al. 1986) and imaging searches for dust comae (Luu & Jewitt 1992). All these searches were negative.

*From comets to asteroids.*

There are numerous examples of comets that ceased to be active. It is now known that only a small part of the cometary nucleus surface is active. In periodic comets, these active areas evoluate with time, with the formation of dust crusts that quench activity, the blowing off of these crusts which exposes ice and initiates new activity (Rickman et al. 1990). This latter may be triggered by thermal cracking of the crust, or by impact cratering by interplanetary small bodies (Hughes 1991). The evolution may be periodic or chaotic. It may be affected, of course, by changes of orbits following planetary perturbations. This can explain the transformation of dormant comets (mistaken for asteroids) into active comets, and the evolution of active comets into extinct comets (which in their turn are alike asteroids). Several asteroids which have orbits similar to short-period comets are supposed to be extinct comets (Hartmann et al. 1987; Weissman et al. 1989).

## Activity of distant comets

This topic, which is obviously related to the preceding one, dramatically came back last year with the discovery of an outburst of P/Halley at 14 AU from the Sun (West et al. 1991; Sekanina et al. 1992). This is not a new topic, since activities of comets at large heliocentric distances were already noted in the past (Meech 1991): for instance, the almost continuous activity of P/Schwassmann-Wachmann 1 at 5-6 AU, the existence of a tail for comet Bowell 1982 I at more than 12 AU.

It is important to assess whether this activity is "explosive" or continuous, if its motor is internal or external. This will not be discussed here. Sublimation of water at these distances is out of the question and very volatile species are required; CO is the one most frequently invoked because it is also abundantly released near the Sun. Others, however, may play an important role ($N_2$, $CH_4$, $CO_2$, $H_2S$, $NH_3$...). Indeed, little clues are available on the molecular content of distant comets: the bands of $CO^+$ and CN are present in the spectrum of P/Schwassmann-Wachmann 1 (Cochran & Cochran 1991; Cochran et al. 1991); CN was detected in Chiron (Bus et al. 1991).

The outgassing from distant comets and asteroids poses interesting problems of hydrodynamics. Compared with what happens at ~ 1 AU, outgassing will occur with a heavier gas (presumably CO instead of $H_2O$), with a lower initial temperature (less than 100 K, possibly 30 K for CO, instead of ~ 180 K). The gas expansion velocity, proportional to $(T/\mu)^{1/2}$, will be smaller: possibly 0.2-0.3 km $s^{-1}$ instead of ~ 0.8 km $s^{-1}$ at 1AU. Photolytic heating, due to its small rate, will be inefficient to accelerate the gas . In the model of Sekanina et al. (1992) for the 14 AU outburst of P/Halley, the retrieved dust expansion velocity is very low (~ 45 m $s^{-1}$), which is hard to explain and is a challenge for dusty-gas dynamics models.

Meech & Belton (1990) and Boice et al. (1992) developed models of the atmosphere of Chiron. The escape velocity may be critical for the dust coma and the largest dust grains may be gravitationally bound; gravity must also be taken into consideration for gas dynamics. The large radius of Chiron (100 to 200 km) also changes the geometry and the time scales, compared to small cometary nuclei. Boice et al. showed that in this case, the gas may be significantly heated by the dust.

## Anisotropic outgassing from the nucleus.

The outgassing from cometary nuclei is not isotropic. This is an expected fact, since the nuclei are not uniformly heated by the Sun: cometary activity occurs preferentially on the sunlit side of the nuclei. An indirect confirmation of this comes from the existence of non-gravitational forces that affect cometary orbits. These forces are attributed to the rocket effect of anisotropic outgassing (Marsden 1968, 1969; Rickman 1989; Yeomans 1991). More direct confirmations came recently with the dramatic images of the circumnuclear region obtained during the fly-by of P/Halley which revealed dust jets and a strong anisotropy of the dust coma. The same evidence can also be obtained from more distant observations: c.f. the Hubble Space Telescope image of comet Levy (Weaver et al. 1992). It is now known that the active areas of cometary nuclei are only a small fraction of their total surface.

Another evidence of the anisotropy of the gas itself comes from the shapes of molecular lines at radio wavelengths (Crovisier & Schloerb 1991) or in the infrared (Larson et al. 1991). The line central velocities are observed to be slightly displaced from the rest velocity of the nucleus, corresponding to a bulk movement of the gas of the order of 0.1-0.3 km $s^{-1}$ toward the Sun.

The problem is that no counterpart of these anisotropies could ever be seen in the brightness distributions of molecular species: from the [OI] lines, which should be a trace of $H_2O$, or from OH, which should keep the memory of any $H_2O$ asymmetry. These distributions seem to be quite isotropic (Festou 1991). Direct mapping of parent-molecule distributions could help resolving this problem in the future. There is also a need for time-dependent 3-D models of dusty gas dynamics to simulate the evolution of gas distribution from sparse active regions (Crifo 1991; Körösmezey & Gombosi 1990).

## Conclusions.

Definite progresses in our understanding of the cometary composition have been made recently, but there are still many open questions. Their answers are needed in order to assess the process of cometary formation and its link to interstellar matter (Greenberg & Hage 1990; Mumma et al. 1992; Despois 1992).

One of the highlights of the *4th Liège International Astrophysical Colloquium* on cometary physics in 1952 was the identification of the 405 nm emission in cometary spectra to the $C_3$ radical. Up to now, the parent molecules responsible for this cometary radical (as well as those responsible for $C_2$) are still the objects of speculations. Another important question is the origin of the *distributed* cometary CO. The mechanism that would allow an important release of CO from CHON grains is still mysterious. The origin of the 3.3-3.5 μm cometary emission band is also still a mystery. The emission bands of methanol and those of PAH can not fully explain this emission. Thermal emission of grains and/or fluorescence of UV-excited large molecules are commonly invoked (Encrenaz & Knacke 1991). We may also speculate that volatile CHO molecules - still to be identified - are responsible for both the lacking 3.3-3.5 μm emission and the production of distributed CO. Limits on the abundances of some of these molecules were recently placed by microwave observations (Crovisier et al. 1992), but all the possibilities have not yet been investigated.

### *Future observations*

Future progresses in this subject will result from both long-term observing programs and the use of new sophisticated techniques.

Systematic searches will undoubtedly reveal other Chiron-type objects. Long-term monitoring of these objects and of distant comets will help us unravelling the mechanisms of their activity at large heliocentric distances. It would be very important to obtain information on the gas composition of distant objects by spectroscopy at all wavelengths, but such observations are very difficult due the weakness of the signal. At least, a confirmation of the CN band in Chiron would be a key experiment.

These last years, investigations of the cometary composition largely benefitted from the development of microwave and infrared spectroscopy. Further progresses are expected from the use of existing ground-based facilities as well as from space infrared telescopes such as ISO (*Infrared Space Observatory*) and SIRTF (*Shuttle IR Telescope Facility*), space submillimetre telescope, either small or large like FIRST (*Far IR Space Telescope*) or LDR (*Large Deployable Reflector*) (Crovisier 1986, 1992). With these latter, one can expect, for instance, an easy study of the strong rotational lines of water and ammonia. We surmise that there is a wealth of cometary volatile components with abundances of the order of 0.1% which are still to be discovered.

A new turn in the study of asteroids and comets may be a sample-return mission like the Rosetta project. We feel, however, that a necessary intermediate step is the study of the cometary environment and the in situ monitoring of cometary activity by a long-lasting cometary exploration mission such as the cancelled CRAF (*Comet Rendezvous Asteroid Flyby*) project.

Finally, laboratory measurements and simulations should be mentionned, for the study of sputtering of molecules and radicals from grains, of photodissociation rates and channels, and of the properties of ice mixtures.

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## DISCUSSION

**G. MARSDEN** - Comment: I think it is important to mention that other researchers have failed to confirm Don Yeoners' computation of nongravitational parameters for Icarus, and he has now withdrawn his claim that nongravitational effects are detectable.

**H. KELLER**: A direct correlation between CN and dust jets has not been established.