

COMETS AS A REFLECTION OF INTERSTELLAR MEDIUM CHEMISTRY

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Abstract. A brief summary of the observed infrared and other properties of interstellar dust is given. Chemical, physical and morphological criteria are discussed concerning the degree to which there are constraints relating comets to interstellar dust chemistry representative of the presolar nebula. Results of theoretical modelling of dust and gas evolution in dense clouds are used to compare with observed dust composition. Sources of the distribution of simple as well as complex molecules in the coma are related to what is presently known about the volatile ices in interstellar dust and to processes leading to evaporation of organic “refractory” grain mantle material represented by laboratory residues produced by photoprocessing of ices. The criterion of preservation of interstellar volatiles in comets leads to the further criterion that the ice in comets is amorphous. Criteria for relating interstellar dust volatiles to asteroids are discussed.

1. Introduction

The chemistry of the interstellar medium is seen in the distribution of the gaseous molecules and in the molecular composition of the dust. The former has been primarily obtained by the use of infrared in the 2.5 μm to 15 μm range. Both of these kinds of observations are direct in the sense that the molecules detected are the molecules present. On the other hand, the chemistry of comets; i.e., the chemical composition of the nuclei of comets, is based on deduction and induction from observations of the volatile and refractory components in the comet coma, both of which have generally undergone considerable changes from their original nucleus abundances resulting from physical and chemical processes after leaving the nucleus. The original or parent comet molecules are seldom observed directly in the coma. Even the most abundant water molecule is mostly studied via its dissociation products OH and H and has been directly observed in only two comets: Halley and Wilson 1987 VII (see Crovisier 1994, this volume and Mumma et al., 1993). Thus the relative abundances of most of the commonly assumed parent molecules are not simply obtained. A major exception is H_2O which is presently believed to be known with sufficient reliability that it is generally used as the reference molecule for all the components of the comet.

There is no general agreement on the degree to which the interstellar dust has been evaporated or modified prior to comet formation. Not all alternatives are reviewed here. Emphasis will be given to those properties of dust and comets, such as the degree of amorphicity of solid H_2O which may impose a strict constraint on whether or to what degree the interstellar dust has evaporated and recondensed.

Even were we to assume that the comet nucleus composition is *exactly* that of the presolar interstellar medium, the question remains what *is* the presolar interstellar medium? There exist neither observations of an interstellar cloud at the stage of

collapse just *before* a star is born nor, as yet, any good theories for the chemistry of the gas and dust in such a very dense cloud. And, as already noted, even if the precometary medium composition were known, the comet nucleus composition is not, at least until there has been a successful comet nucleus sample return mission.

The problem, then, of establishing a precise correspondence between presolar chemistry and comet composition involves, in the former, a forward extrapolation from observed conditions before star formation or a backward extrapolation of the medium after star formation, and for the latter, a time reversed extrapolation of the composition in the comet coma.

The correspondence between molecular abundance ratios in comet nuclei and in the interstellar medium out of which they are formed is thus fraught with potential pitfalls. *Both* the chemistry *and* the morphology of the interstellar dust are needed to provide the connections to comet nuclei.

In this paper we consider both refractory and volatile components of the comet nucleus. It is important to do this because they are not entirely separate. First, there is a wide range of volatility in the so-called refractory dust components and secondly, some of the simple molecules of the gaseous coma are derivatives of complex dust organic "refractory" molecules and not daughters of frozen cometary volatiles. With this caveat in mind we shall begin by summarizing some of the known properties of interstellar gas and dust with emphasis on those aspects which seem most likely to bear on comet chemistry.

One of the clues indicating the proper approach to be taken is the H₂O to CO ratio in molecular clouds and in comets. While it is well known that CO is by far the most abundant gas phase molecule in the interstellar medium (obviously excepting H₂) it is substantially less abundant in the comet coma than H₂O. On the other hand *solid* H₂O is the most abundant mantle molecule on the interstellar grains, generally exceeding CO by a factor of 5 or more. It is therefore logical to place particular emphasis on the interstellar *dust* molecules both as observed and as deduced from dust/gas cloud chemistry as an initial basis for considering comet composition.

2. Interstellar Cloud Chemistry

We shall first summarize some of the observational evidence for the molecular abundances in grains. Next we shall give an example of a dust/gas chemistry scheme which provides a basis for explaining simultaneously the dust mantle and gas phase abundances.

2.1. INTERSTELLAR DUST OBSERVATIONS

2.1.1 Refractory components :

Silicates :

In diffuse interstellar clouds the dust consists of at least three and possibly four separate components differing in both size and chemical composition. The major fraction by mass is in the particles whose mean size is in the order of one tenth micron. These particles consist of a core of silicates which is both amorphous and elongated- a seeming contradiction in properties. Nevertheless, observations of the

excess polarization produced by interstellar dust in the $9.7 \mu\text{m}$ Si-O stretch band as seen, for example, in the Orion BN source (see Whittet, 1992 for a review) and in other sources as well show that the silicate is elongated (certainly nonspherical). Furthermore this band has the width characteristic of a generalized amorphous silicate (Day, 1979). It has been conjectured that, although the material is indeed amorphous, it is elongated by virtue of consisting of two or several particles which somehow stick together, when formed in the atmosphere of cool evolved oxygen rich stars (Greenberg, 1989). The fact that the H_2O ice band (see later) also exhibits excess linear polarization indicates that it forms as a mantle on the silicate (Dyck and Lonsdale, 1981). Observations of the abundances of Si, Mg, and Fe in the clouds indicates that of the order of 95% of these elements are found in the amorphous silicates. Although the $9.7 \mu\text{m}$ absorption is always observed where interstellar extinction exists, the cosmic (solar system) abundances of the rocky elements (Si, Mg, Fe) is insufficient to provide, as particulates, the observed total extinction (Spitzer, 1978; Greenberg, 1991a). An additional component is required (see next).

The organic refractory component :

In diffuse clouds an insufficiency of rocky elements to produce the observed amount of interstellar extinction by silicates alone, suggests that mantles of the organics - OCN elements - must be involved. If one examines the spectrum toward the galactic center, the silicate feature far outweighs any evidence for mantles - certainly the ice band is absent. But the apparently insignificant (with respect to the "normally" strong ice bands) feature at $3.4 \mu\text{m}$ characteristic of CH stretches in organic mixtures is *the* evidence for the organic mantle needed. Spectroscopically it compares well with that of the organic residue which results from long term laboratory photoprocessing of ices (Schutte and Greenberg, 1986; Sandford et al, 1991). These molecules are presumed to be created in molecular clouds by photoprocessing of the ices. It was predicted that such a mantle material should be observed wherever the ice band is not present (Greenberg, 1973) and has now been observed not only towards the galactic center but also towards the object for which it was originally predicted, namely VI Cygni# 12 (Sandford et al. 1991). In order to account for the observed continuum properties of interstellar dust using silicates and organic refractories alone in the diffuse interstellar medium a mass ratio of organic to silicates of the order of one is required (Greenberg, 1982b). One would expect the organic refractory dust mantle to be little changed when the diffuse cloud dust accretes a volatile icy mantle in the molecular cloud phase. The absence or reduction of the $3.4 \mu\text{m}$ feature in the extended line of sight toward protostellar objects (Allamandola et al. 1992) applies to molecular cloud material which has undergone various degrees of processing (heating, etc.) following star formation and it would certainly be a puzzle if it could also be demonstrated for prestellar molecular cloud dust as seen toward, say, Elias 16.

Small carbonaceous : The smaller ($\leq 0.01 \mu\text{m}$) particulates which are variously suggested to provide primarily the ultraviolet extinction are all carbon rich (Jenniskens et al, 1993). Their abundances are not well established but it has been suggested that between ≈ 5 and 10% of the total available carbon is contained in large polycyclic aromatic hydrocarbons (PAH's) (Allamandola et al., 1989) and as much as $\approx 20\%$ of the carbon is required to account for the 220 nm extinction

(absorption) bump (Greenberg, 1982a).

2.1.2 Volatile ice components :

The volatile components of interstellar dust are no more uniformly observed than the gaseous components in molecular clouds. However, just as CO is a ubiquitous gas phase molecule whose abundance in a variety of clouds is high and rather uniform so H₂O ice is the most generally observed volatile molecule in the dust. In the following we will briefly summarize the observational evidence for the ice mantle molecules.

H₂O :

Water ice has now been observed in a wide variety of astrophysical regions. It was first observed in the Orion BN-KL source and since then in many other regions of new star formation as well as in more normal clouds. Its most generally observed feature is at about 3.07 μm . The 6 μm feature is not as frequently observed and the 12 μm feature is blended with the 9.7 μm silicate feature making it difficult, but not impossible, to derive molecular abundances. Not all the interpretations of the observations agree with respect to the actual abundance of the H₂O molecule. This is partially because the effects of mixtures of other molecules on the 3.07 μm H₂O absorption strength and also the effect of the *particle shape* on the band *absorption shape* are not usually considered, as, for example in van de Bult et al. (1984). The excess polarization at 3.07 μm shows in Elias 16 as in BN that the ice has a non spherical form. The optical depth relative to the extinction of $\tau_{3.07}/A_v = 0.059 \pm 0.003$ obtained by Smith et al. (1993) in the Taurus dark cloud yields an [H₂O/H] ratio of $\simeq 5 \times 10^{-5}$, using $A_v/N_H = 0.5 \times 10^{-21}$, $\sigma_{H_2O} \simeq 6 \times 10^{-19} \text{ cm}^2$. The solid H₂O optical depth at 3.07 μm is reduced in an ice mixture because of the diluting presence of nonpolymeric H₂O. This reduction has been estimated to be as much as by a factor of the order of 0.5 for a fractional ice composition of 60% (Greenberg, 1982b) so that the solid H₂O estimate in the above cloud could be as high as 10^{-4} . The H₂O seen through the cool molecular cloud towards Elias 16 is well characterized by an ice band which matches that for non-spherical grain models with amorphous ice mantles (van de Bult, Greenberg and Whittet, 1984). Its abundance is [H₂O/H] = 7×10^{-5} is compared with 2×10^{-5} for gaseous CO along the same line of sight and with 1×10^{-5} solid CO (Tielens et al, 1991). We do not here generally consider protostars or YSO (young stellar objects) spectra as representative of interstellar dust for comets because there is considerable modification of the relative proportions of the various components caused by heating following star formation. This is particularly true for CO which evaporates much more readily than the H₂O. Although, as pointed out by Tielens and Allamandola (1987), the optical depth at 3.07 μm may be less reliable than that at 6 μm for obtaining H₂O abundances it is much more frequently observed and provides a far greater data base. In any case, the fact that H₂O is the most abundant solid phase molecule turns out to be unambiguously clear. The generally accepted amorphicity of the ice in comets provides a constraint on its origin as interstellar ice mantles. It has been demonstrated that if the dust ice is evaporated and recondensed in the solar nebula it would be crystalline even at relatively low temperatures (Kouchi et al, 1993).

CO :

Again considering the Taurus molecular cloud, the solid CO abundance is less than the solid H₂O abundance, as already noted by Whittet et al. (1988) and as since confirmed by many later observations (see Whittet and Duley, 1992 for a review). It is also very clear that in such objects as in Orion near young hot stars (Geballe, 1986) and in W33A the solid CO is substantially reduced (Lacy et al., 1984) undoubtedly as a result of heating of the dust (Schmitt et al., 1989). This will be shown in the later discussion of the OCN⁻ ion. In Elias 16 the solid CO abundance is $[CO/H] \approx 1 \times 10^{-5}$ so that the water to CO ratio is $[H_2O/CO] \approx 7$; i.e. about 15% CO. In no case has a solid CO abundance exceeded the solid H₂O whereas in the gas phase $[CO/H_2O] \geq 10$. We should point out that the gas phase H₂O is exceedingly difficult to measure. The low value is, however, confirmed by theoretical dust/gas modelling as well as by pure gas phase interstellar cloud modelling (van Dishoeck et al., 1993) as will be shown explicitly shown later.

CO₂ :

The detection of the solid CO₂ by its CO stretch is made difficult because of the atmospheric absorption by gaseous CO₂. However its bending mode absorption at 15.2 μm is not so obscured. Nevertheless, being on the edge of the broad H₂O 12 μm absorption has prevented its clear detection. By a very difficult subtraction procedure using the IRAS Low Resolution Spectra d'Hendecourt and de Muizon (1989) made the first discovery of the solid CO₂ by comparison with laboratory spectra. While the detection has not been made for normal molecular cloud dust, there is abundant laboratory data on the ultraviolet irradiated interstellar ice samples containing H₂O and CO, which show that CO₂ *must* be present in molecular cloud dust (d'Hendecourt et al. 1985; Greenberg and d'Hendecourt, 1985). Its abundance by laboratory data as well as by the limited observation is possibly as high as CO.

CH₃OH :

Observations of the 3.53 μm and 9.8 μm CH₃OH bands toward various embedded protostellar objects give widely varying abundances of CH₃OH relative to H₂O in interstellar ices; i.e., between 4% and 40% (Grim et al, 1991; Schutte et al, 1991; Allamandola et al, 1992; Skinner et al, 1992, Schutte et al, 1994). Thus although the presence of methanol in dust is well demonstrated its abundance in precometary dust is not yet demonstrated. Note that methanol has not yet been discovered in *normal* molecular clouds but this would be an observational selection effect because it is made in or on the dust (see section on dust/gas modelling). In fact theoretical dust/gas modelling (see Table II) indicates that methanol is probably not very abundant in *fairly* dense clouds which are still at a stage of *pre*-protostellar cloud contraction.

H₂CO :

It is only very recently that formaldehyde has been detected in interstellar dust even though it, like methanol and carbon dioxide, must be created by photoprocessing of dust ice mantle mixtures or possibly by surface reactions (Tielens and Hagen, 1982). Its abundance in the source of AFGL 2136 has been estimated as about comparable with CH₃OH; i.e. about 3% (Schutte et al, 1994). The region of the observation is not a simple molecular cloud because the source is a deeply embedded object, a YSO.

NH_3 , CH_4 :

In spite of the fact that NH_3 and CH_4 are expected to be substantially represented in the interstellar ice mantles in molecular clouds, particularly in young clouds, neither one can claim to be *quantitatively* detected. Early claims for the NH_3 abundance were not justified by later interpretation of the spectral features at about $2.95 \mu\text{m}$ although the expected induced long wavelength wing of the $3.07 \mu\text{m}$ ice band is consistent with a fractional abundance of about 10% (van de Bult et al., 1984). The methane molecule has only been observed in deeply embedded sources and, in the solid phase, may there be even more abundant than CO. But note that CO has a higher vapour pressure and for heated dust a starting ratio of $[\text{CO}/\text{CH}_4] > 1$ could be inverted. Since CO is relatively depleted in W33A it is not surprising that for this source CH_4 is significantly more abundant (Lacy et al., 1991). In any case, the fact that CH_4 can even be comparable with CO in the solid shows that it is produced most likely on the dust rather than in the gas phase where $[\text{CH}_4/\text{CO}]$ is typically $\approx 10^{-3}$. Thus CH_4 is like H_2O , produced predominantly as a solid whereas CO is produced primarily in the gas and *then* accreted.

OCS :

This sulphur molecule has been observed in W33A - again a deeply embedded object rather than a dense molecular cloud (Geballe et al., 1985; Grim and Greenberg, 1987a). Nevertheless, the deduction from the laboratory comparisons would indicate that this molecule should also be present in significant amounts in molecular clouds. In laboratory experiments H_2S was used to produce OCS (Grim and Greenberg, 1987a) but the original evidence for H_2S has been shown to be incorrect (Allamandola et al., 1992).

OCN^- , NH_4^+ :

These ions are put together because they probably form as counter ions as a result of photoprocessing of dust mantles. The OCN^- : CO ratio is much higher in W33A (a heated region) than in NGC7538 IRS9 (Grim and Greenberg, 1987b; Grim et al., 1989). The latter is probably closer to prestellar dust.

2.2. INTERSTELLAR DUST/GAS : THEORETICAL AND LABORATORY MODELLING

A series of paper originating in Leiden have examined the combined time dependent evolution of gas and dust (Tielens and Hagen, 1982; d'Hendecourt et al., 1985; Breukers, 1991) taking into account surface reactions, ultraviolet photoprocessing of the dust and explosive desorption of volatile dust mantles. The most recent effort in this direction has explicitly examined photoprocessing of the interstellar mantle molecules with the aim of following the development of such molecules as H_2CO and CH_3OH as well as the more common molecules (Shalabiea and Greenberg, 1993). Not only are the predicted gas phase molecules in better agreement with observations but the dust mantle molecules are also well represented. We repeat the caveat already expressed earlier that although the calculations have been performed for fairly dense interstellar clouds they have not yet been carried through the phase in which the cloud collapses toward the protosolar nebula phase. Nevertheless the results are encouraging both in comparison with interstellar dust observations *and* comet coma observations. We shall summarize below the results of laboratory and theoretical studies of interstellar dust and interstellar gas.

2.2.1 Molecular Gas and Dust : Theoretical modelling

The basic physical processes considered, in addition to the usual gas phase interactions, are surface reactions, accretion, photoprocessing and dust explosive desorption. A total of 217 molecular species and 2074 individual reactions are included. The cloud density is $n_0 = n_{\text{H}} + 2n_{\text{H}_2} = 2 \times 10^4 \text{ cm}^{-3}$ where most of the hydrogen winds up as H_2 . Solid state photoproduction of three crucial molecules CO_2 , H_2CO and CH_3OH are specifically included basing their photoproduction on laboratory results. In table I are given some of the calculated gas phase species compared with their observed values and with values calculated without including dust. This table is presented to show how the theory, including the dust as we have done in the total chemical scheme, provides a more reliable set of values than that using gas phase reactions alone.

We note in particular, that the gas phase abundances of H_2CO , CH_3OH and CH_4 are an order of magnitude or more greater when the dust is included in the reaction scheme and that they are then closer to the observed values. A detailed discussion of all parameters involved in the chemical scheme is beyond the scope of this paper. For details see Shalabiea and Greenberg (1993). Of more direct relevance is the dust mantle composition. The theoretical derived dust mantle components are presented in table II for the two dust/gas models (low photoproduction and high photoproduction) represented by their gas phase abundances in the two right columns of Table I.

Table I: Some steady state molecular gas abundances using pure gas phase reactions and combined dust/gas reactions. Cloud density $n_0 = 2 \times 10^4 \text{ cm}^{-3}$, $T_d = T_G = 10\text{K}$. Low and high p.p. refer to high and low solid state photoproduction rates estimated from laboratory results. Two cosmic ray ionization rates, ζ , are used.

	Observed		Gas alone		dust/gas ($\zeta = 5(-17)$)	
	L134N ^a	BN ^b	$\zeta = 1(-17)$	$\zeta = 5(-17)$	low p.p.	high p.p.
CO	8(-5)	1(-4)	1.5(-4)	1.6(-4)	7.0(-5)	6.8(-5)
H ₂ O	–	1(-5)	3.2(-6)	9.7(-6)	5.8(-6)	6.1(-6)
H ₂ CO	2(-8)	>6(-8)	1.1(-9)	2.3(-9)	2.9(-8)	2.7(-7)
CH ₃ OH	2(-9)	0.1-1(-6)	7.4(-11)	3.9(-10)	2.6(-9)	1.3(-7)
NH ₃	3(-8)	1(-7)	5.1(-9)	1.5(-8)	1.5(-7)	1.5(-7)
CH ₄	–	1(-7)	9.7(-9)	1.3(-8)	1.3(-7)	1.0(-7)
HCN	1(-8)	–	6.5(-9)	3.0(-9)	2.0(-8)	3.0(-8)

^a see van Dishoeck et al., 1993 for the cloud L134N

^b see van Dishoeck et al., 1993 for Orion BN/ext. ridge

We see that the predicted ratio of the CO to H₂O is $\leq 1/4$ in the solid while, in the gas, the predicted ratio is > 10 . Furthermore the formaldehyde and methanol

fractions- relative to H_2O - are generally an order of magnitude greater in the dust than in the gas *and* since the H_2O in the solid is much higher than in the gas this represents at least *several* orders of magnitude improvement as compared with the values observed in the comet coma. Note that the methanol to water ratio is much lower and its CO to water ratio is much higher than in W33A but also note that if *this* dust (in table II) were to be heated not only would the CO be reduced but a substantial portion of the formaldehyde would likely be converted to methanol (Zhao, 1990). Also of interest is the CH_4 : CO ratio in the dust in relation to that observed in the comet and that predicted by solar nebula chemistry, assuming all the dust volatiles have evaporated before comet nuclei formation. From table II, $\text{CH}_4/\text{CO} = 0.01$ to 0.0007 which is outside the observed ratio range for comet Halley ($0.03 - 0.17$) but is orders of magnitude closer than the solar nebula disequilibrium calculations prediction of $\text{CH}_4/\text{CO} < 10^{-7}$ (Prinn and Fegley, 1989; Fegley and Prinn, 1989).

Table II. Solid state dust mantle abundance fractions of several key molecular species resulting from theoretical time dependent chemistry at steady state in a cloud with $n_0 = 2 \times 10^4 \text{ cm}^{-3}$ and ionization rate $\zeta = 5 \times 10^{-17} \text{ s}^{-1}$

	low p.p	high p.p
CO	0.18	0.15
H_2O	0.70	0.58
H_2CO	0.01	0.15
CH_3OH	0.001	0.02
NH_3	0.008	0.008
CH_4	0.002	0.0001

2.2.2 Laboratory Produced Organic Residues :

A laboratory analog of the photoprocessing of interstellar ices lead, after warmup, to organic residues which are presumed to resemble the organic refractories which are observed by their $3.4 \mu\text{m}$ absorption. The chemical characteristics of the laboratory organics is taken as a first approximation to interstellar organic mantles. GCMS analysis shows that it consists in part of many prebiotically significant molecules (Briggs et al., 1992), the most abundant having been determined to be approximately 7% ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), 30% glycolic acid ($\text{HOCH}_2\text{CO}_2\text{H}$), 21% 2-hydroxyacetimine ($\text{HCCH}_2\text{CONH}_2$), 3% urea (NH_2CONH_2), 6% glycerol ($\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$), 7% glyceric acid ($\text{HOCH}_2\text{CH}(\text{OH})\text{CO}_2\text{H}$) and 19% glyceramide ($\text{HOCH}_2(\text{OH})\text{CONH}_2$). Mass spectroscopic analysis of a residue has revealed masses up to ~ 1000 and identifications of both aliphatic and aromatic hydrocarbons have been obtained. These new results indicate the presence of highly unsaturated, aromatic hydrocarbons (see table III). This agrees qualitatively with what has been found for meteoritic material (Grady et al., 1983; Gilmour and Pillinger, 1985) and cometary material (Kissel and Krueger, 1987; Mukhin et al., 1989). The most refractory part of the organic residue material consists of relatively

high molecular weight (≥ 400 AMU) polymers, which have not yet been completely characterized.

Finally, we also studied the volatile part by means of a gas collector (Mendoza-Gómez, 1992). Once the initial gas mixture ($\text{H}_2\text{O} : \text{CO} : \text{NH}_3 = 5 : 5 : 1$) was irradiated at 12K, the sample was slowly warmed up, and the material coming off was trapped with a gas collector between given temperatures. The results found for materials coming off from 100 K to room temperature are shown in table IIIb. It is interesting to note how little nitrogen is contained in the intermediate masses shown here compared with the compounds discussed earlier (Briggs et al., 1992). Coincidentally, nitrogen appears to be underabundant in comet volatiles (Wyckoff et al., 1991) and may possibly be embedded in the highly polymerized fraction which in our residue has not yet been analyzed. These new results further confirm comet origins as being the interstellar dust.

Table III. (a) High-resolution fast atom bombardment mass-spectral data of the organic refractory residues (U.V. irradiated $\text{H}_2\text{O} : \text{CO} : \text{NH}_3 = 5 : 5 : 1$), (b) High resolution electron mass-spectral data of the gas material collected from 100K to room temperature

Mass no. (a)	elemental composition	Mass no. (b)	elemental composition
219	$\text{C}_{14}\text{H}_{19}\text{O}_2$	44	CO_2
203	$\text{C}_{14}\text{H}_{19}\text{O}$	44	$\text{C}_2\text{H}_4\text{O}$
189	$\text{C}_{13}\text{H}_{17}\text{O}$	70	$\text{C}_4\text{H}_6\text{O}$
173	$\text{C}_{13}\text{H}_{17}$	84	$\text{C}_5\text{H}_8\text{O}$
159	$\text{C}_{12}\text{H}_{15}$	98	$\text{C}_6\text{H}_{10}\text{O}$
157	$\text{C}_{12}\text{H}_{13}$	103	$\text{C}_7\text{H}_5\text{N}$
		115	$\text{C}_7\text{H}_17\text{N}$
		116	C_9H_8

It is possible that in some astrophysical situations, when the dust is heated in the presence of protostellar sources, these intermediate size molecules are evaporated and become mixed with the gas.

Some of the molecules identified using high resolution (elemental compositions), MS/MS mass spectral data (mass spectra of individual peaks) and direct comparison with mass spectra of model compounds are shown below in Figure 1. Note how cyclic compounds seem to be well represented. This is encouraging because polycyclic aromatics appear to require a source in the interstellar medium (Greenberg et al., 1992) rather than circumstellar as often suggested. Indeed there is also evidence for a polycyclic aromatic phenanthrene (Moreels et al., 1993), in comet Halley spectra which would be similar to the $m/z = 214$ labeled molecule in Figure 1.

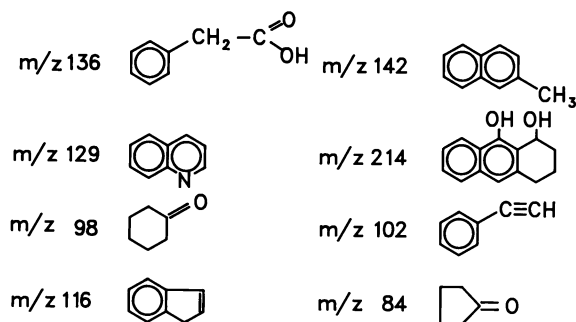


Fig. 1. Identified cyclic molecules in organic residue.

3. Physical Description of Comet Dust

3. 1. POROSITY OF INTERSTELLAR DUST AGGREGATES DERIVED FROM COMET HALLEY DATA

A detailed calculation was performed for the dust of comet Halley (Greenberg and Hage, 1990) in which it was shown that the interstellar dust model for the coma consisting of silicate core-organic refractory mantles (volatiles like H_2O etc. have been depleted in the coma dust) can both simultaneously and quantitatively fulfill the observational constraints of: (1) the observed strength of the 3.4 and 9.7 μm emission bands; (2) the *shape* of the 9.7 μm band; (3) the relative amounts of silicates to organic materials measured in situ; (4) the mass distribution of the dust *if* the coma dust is a fluffy aggregate at least as porous as $P = 0.93$ and with a likely porosity as high as 0.975; i.e. 97.5% empty space. The organic refractories not only provide a source of the 3.4 μm emission, they are *absolutely required* to heat the dust, *otherwise* the 9.7 μm emission would not exist because silicates do not absorb enough solar radiation to achieve the *above* black body temperature needed for the excess *spectral* emission. The key words here are *above black body temperature!* Very fluffy comet dust can approach the absorption/emission properties of a *cloud* of tenth micron core-mantle dust particles whose temperatures can greatly exceed the temperatures of the aggregated particles considered as compact. One should not automatically assume that such dust has no rigidity because some rigidity is already shown by aerogels with porosity as high as or higher than 0.99. The coma dust temperature for a basic core-mantle grain with partial organic refractory evaporation ($\text{Si}/\text{O.R.} \approx 2$) at 0.98 au from the sun is 560K as compared with about 290K black body temperature. A fluffy aggregate of such particles with $P = 0.95$ and overall size 2.5 μm would be at $T \approx 500\text{K}$ whereas as a *solid* particle with the same mass its temperature would be only $\approx 300\text{K}$. However, for particles as large as 50 μm (mass $\approx 5 \times 10^{-8}$ g) the temperature is down again to $T \approx 310\text{K}$.

3. 2. SOURCES OF SIMPLE COMA SPECIES IN THE DUST ORGANICS

While the emphasis in the past was to try to identify the volatile molecules as parents of coma molecules it is now well recognized that a significant number of daughter molecules have as their source the relatively nonvolatile organic species which are part of the dust. What is the source of C_2 and C_3 which Crovisier (this volume) denotes as orphan molecules for which no specific parent has been identified? We believe that the answer must lie in the existence of the organic refractory interstellar dust mantles. We shall discuss this both from the point of view of observed infrared properties of comet dust as well as the laboratory analog results on simulated interstellar organics. There is also a recent and important observation of a new comet Yanaka 1988r for which the conspicuous absence of C_2 and CN may be used to infer *why* they must arise from dust organic refractories. We shall first present a brief summary of an interstellar dust model of comet dust from which it may be shown *physically* how the organics provide a source of volatiles in the comet coma which is continuously distributed as the dust clouds expands away from the nucleus. We shall show also how some of the identified laboratory produced organics may be evaporated, dissociated or pyrolyzed to produce the observed (range of) abundances of such species as C_2 , CN as well as CO.

The smaller components in the organic refractory component generally have higher vapor pressures than the hydrocarbon species detected by mass spectrometry, some of which are large polymers. In general the temperatures at which pyrolysis occurs in these components is typically $T \geq 410\text{K}$ (Briggs et al, 1992). Since sufficiently large particles - even fluffy ones - approach the black body temperature, we expect that only a limited size (mass) range of particles in the comet dust distribution can contribute substantially to distributed volatiles. The fact that there is a substantial fraction of complex organics in comets (and comet dust) is thus a *necessary* but not *sufficient* condition for providing a distributed source of CO, C_2 , CN etc. This question of the required porosity was first semi-quantitatively considered by Greenberg and Hage (1990) in the production of CO. By imposing the lower limit $T \geq 410\text{K}$ we can refine this by noting that : 1) the total possible CO mass fraction source in the volatile organics is about 0.3 (see the list of molecules identified in the laboratory residues as the organic refractories which contain CO groups), and 2) the volatile organics constitute (originally) about 1/3 of the total dust mass. Using these refractories we find - based on the dust temperature calculations of Greenberg and Hage (1990) - that the maximum *distributed* CO production rate is $M(\text{CO}) \approx 0.3 \times 10^5 \text{ g s}^{-1}$ for $M_d (< 10^{-8})$; i.e. a factor of at least 30 times more dust than that limited to $M_d < 10^{-8} \text{ g}$ would be needed to account for the required CO distributed production rate of $8 \times 10^5 \text{ g s}^{-1}$ as in Eberhardt et al (1987). This requires particles with $P \geq 0.975$ to provide the temperature $T \geq 400 \text{ K}$ for the particle masses up to $m \approx 3 \times 10^{-7} \text{ g}$ which would *just* provide the distributed CO. Thus in order to make a good case for organic (semi)refractories being the source of such distributed molecules as CO, CN, etc., high porosity is critical to achieve the high temperatures needed to evaporate the parent organic molecules as a sufficient source of the distributed molecules. Furthermore the farther out in the coma one looks, the higher the mean dust temperature because of more and more small particles so that a substantial fraction of the total dust could be a

temperature approaching that of individual core-mantle particles. This makes for distributed molecules from more refractory organics being made possible; e.g., CN is generally in more refractory components than is CO.

3. 3. DUST PROPERTIES NEAR A NEW COMET NUCLEUS DERIVED FROM COMET YANAKA 1988R :

We have comet Yanaka (1988r) as an example of what happens to the source of distributed molecules if the dust is limited to large cool particles. A deficiency in the observed abundances of C₂ and CN in the comet may be explained in terms of the properties of its organic refractory components plus the fact that it is a new comet *and* the small aperture (very close to the nucleus) with which it was observed. First of all, the parent source of C₂ and CN is relatively tightly bound within the comet dust whose outer layer has been processed by cosmic rays while in the Oort cloud (Strazzulla and Johnson, 1991). Secondly, the cosmic-ray-processed dust is less fragile (is better glued together because the volatile ices are converted to organics) than that of a periodic comet so that its size distribution is weighted toward larger cooler particles than those of an old comet. The coma dust from the outer crust is probably also less porous because it has far less volatiles to be evaporated. Finally, the small central observation diaphragm further exaggerates the size distribution effect by not allowing time for fragmentation to occur. The consequent low surface-to-mass ratio and the relative coolness of the dust *within* the regions of observation of comet Yanaka (1988r) combined in a nonlinear way to inhibit severely the "usual" sources of C₂ and CN. It is worth noting here that the weakness of the 3.4 and 9.7 μm excess emissions in another dynamically new comet also observed with small aperture (Hanner et al, 1993) are consistent with the suggestions for the dust properties of comet Yanaka(1988r).

4. Asteroids and meteorites

The connection between interstellar chemistry and asteroids is at least one step removed from that with comets; and it is a further step to meteorites which are asteroidal debris. Among other things the region where asteroids are formed and their subsequent temperature history precludes that water could have survived in solid form. The evidence that liquid water was incorporated in asteroids is suggested as a reason for the layer-lattice silicates in those IDP's (interplanetary dust particles) which appear to be debris of asteroids, such silicates resulting from hydration in the presence of liquid water (Sandford, 1991). Was this water melted interstellar ice or was it water which had formed in the solar nebula after the dust evaporated? The answer to this may depend on the apparent correlation between the abundance of carbonates and layer-lattice silicates in meteorites (Greenberg, 1991b) . The formation of carbonates implies the presence of a significant amount of CO₂ in solution. The question is where does the required amount of CO₂ originate? The abundance of CO₂ in interstellar dust is substantial - probably of the order of that of CO (about 5% ,or more, relative to that of H₂O)- but in models of solar nebula chemistry it is at least ten times less(Fegley,1993; Prinn,1993). On this basis one would need to attribute the carbonic acid as forming from dissolved interstellar

CO₂ brought in with the interstellar ice which has melted in the interior of the asteroid. A further connection has been suggested by Cronin and Chang (1993) via the organic rich CI1 and CM2 carbonaceous chondrites which contain minerals also (as in the IDP's) believed to indicate hydrous activity in the meteorite parent body. The organic chemistry of these meteorites and the substantial deuteration of their organic compounds as well as enrichment in ¹⁵N and in ¹³C relative to terrestrial matter are "consistent with a formation scheme in which (1) a parent body was formed from volatile-rich icy planetesimals containing interstellar organic matter, (2) warming of the parent body led to an extensive aqueous phase in which the interstellar organics underwent various reactions, and (3) residual volatiles were largely lost leaving behind the suite of nonvolatile compounds that now characterize these meteorites." Thus a simultaneous correlation of substantial organics, layer-lattice silicates, carbonates and isotopic enrichments would go far toward establishing an asteroid-interstellar dust connection.

5. Conclusions

It has been shown that not only the volatiles (ices) of interstellar dust are related to comet coma molecules but also the organic refractory components. Preservation of volatiles in comets in approximate proportions to those observed or inferred for prestellar interstellar dust appears to preclude their evaporation before comet nucleus formation. Further evidence is given showing that the criteria for distributed molecules from the refractory component are that the comet dust and, by inference, the comet nucleus be extremely porous. A requirement of $P > 0.975$ on the comet dust leads to a nucleus density of $< 0.3 \text{ cm}^{-3}$ consistent with the values derived by Rickman (this volume). The amorphous property of H₂O ice in comet nuclei can be attributed *only* to the amorphous ice in interstellar dust because ice condensed in the solar nebula would have to be crystalline.

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