ORGANIC MOLECULES IN THE INTERSTELLAR MEDIUM, COMETS, AND METEORITES: A Voyage from Dark Clouds to the Early Earth

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■ **Abstract**   Our understanding of the evolution of organic molecules, and their voyage from molecular clouds to the early solar system and Earth, has changed dramatically. Incorporating recent observational results from the ground and space, as well as laboratory simulation experiments and new methods for theoretical modeling, this review recapitulates the inventory and distribution of organic molecules in different environments. The evolution, survival, transport, and transformation of organics is monitored, from molecular clouds and the diffuse interstellar medium to their incorporation into solar system material such as comets and meteorites. We constrain gas phase and grain surface formation pathways to organic molecules in dense interstellar clouds, using recent observations with the Infrared Space Observatory (ISO) and ground-based radiotelescopes. The main spectroscopic evidence for carbonaceous compounds in the diffuse interstellar medium is discussed (UV bump at 2200 Å, diffuse interstellar bands, extended red emission, and infrared absorption and emission bands). We critically review the signatures and unsolved problems related to the main organic components suggested to be present in the diffuse gas, such as polycyclic aromatic hydrocarbons (PAHs), fullerenes, diamonds, and carbonaceous solids. We also briefly discuss the circumstellar formation of organics around late-type stars.

In the solar system, space missions to comet Halley and observations of the bright comets Hyakutake and Hale-Bopp have recently allowed a reexamination of the organic chemistry of dust and volatiles in long-period comets. We review the advances in this area and also discuss progress being made in elucidating the complex organic inventory of carbonaceous meteorites. The knowledge of organic chemistry in molecular clouds, comets, and meteorites and their common link provides constraints for the processes that lead to the origin, evolution, and distribution of life in the Galaxy.

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1.   INVITATION TO THE VOYAGE

The interstellar medium (ISM) consists of gas and dust between the stars, which accounts for 20–30% of the mass of our galaxy. Much of this material has been ejected by old and dying stars. The ISM contains different environments showing large ranges in temperature (10–10^4 K) and densities (100–10^8 H atoms cm^{-3}). It is filled mainly with hydrogen gas, about 10% helium atoms, and $\sim$0.1% of atoms such as C, N, and O. Other elements are even less abundant. Roughly 1% of the mass is contained in microscopic (micron-sized) dust grains. The interstellar medium represents the raw material for forming future generations of stars, which may develop planetary systems like our own. Comets and carbonaceous chondrites may be witnesses of the processes occurring during the gravitational collapse of molecular clouds to form stars and protoplanets. There is evidently a link between chemical processes in dark embedded clouds and cometary volatiles; a detailed elucidation of the connection between interstellar, cometary, and meteoritic dust can provide constraints on the formation of the solar system and the early evolution of life on Earth (Irvine 1998).

Astronomical observations of the ISM and solar system bodies, in combination with laboratory investigations of meteoritic samples, have shown the presence of numerous organic molecules. Well over one hundred different molecules have been identified in interstellar and circumstellar regions, most of them are organic in nature (see Table 1; see also http://www.cv.nrao.edu/~awootten /allmols.html). Larger carbon-bearing species such as polycyclic aromatic hydrocarbons (PAHs) and fullerenes may also be present in interstellar gas or incorporated in dust and ice mantles. A large amount of the cosmic carbon is locked in carbonaceous solids on dust grains.

Dense clouds are characterized by very low temperatures (10–30 K) and high densities (10^{4-8} hydrogen atoms cm^{-3}). Cold gas phase chemistry can efficiently form simple species such as CO, N_2, O_2, C_2H_2 and C_2H_4, HCN, and simple carbon chains (Herbst 1995). Efficient accretion of atoms and molecules in such environments and subsequent reactions on the grain surface lead to the formation of molecules such as CO_2 and CH_3OH, which are later returned to the interstellar gas (Tielens & Hagen 1982, Schutte 1999). Evaporated ices can drive gas phase reactions by acting as precursors for the larger organics that are observed in hot cores (Charnley et al 1992). The largest organic molecule that has been unambiguously identified in the interstellar gas is $HC_{11}N$ (Bell et al 1999). The tentative detection of diethyl ether [$(C_2H_5)_2O$] has also been recently reported (Kuan et al 1999). The chemistry in interstellar clouds and the production of organic molecules can be enriched by thermal and energetic processing, such as ultraviolet (UV) irradiation and cosmic rays. Although the UV radiation field of a young protostar is strongly attenuated within its close environment, cosmic rays can penetrate throughout the cloud and ionize H_2 molecules; the energetic electrons from these molecules can in turn excite H_2 to higher electronic states. These excited H_2 molecules subsequently

TABLE 1 Interstellar and circumstellar molecules as compiled by Al Wootten (see text)

						Number of Atoms					
2	3	4	5	6	7	8	9	10	11	13	
H_2	C_3	$c\text{-}C_3H$	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H	$CH_3C_5N?$	HC_9N	$HC_{11}N$	
AlF	C_2H	$l\text{-}C_3H$	C_4H	$l\text{-}H_2C_4$	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH_3)_2CO$			
$AlCl$	C_2O	C_3N	C_4Si	C_2H_4	CH_3C_2H	$CH_3COOH?$	$(CH_3)_2O$	$NH_2CH_2COOH?$			
C_2	C_2S	C_3O	$l\text{-}C_3H_2$	CH_3CN	HC_5N	C_7H	CH_3CH_2OH				
CH	CH_2	C_3S	$c\text{-}C_3H_2$	CH_3NC	$HCOCH_3$	H_2C_6	HC_7N				
CH^+	HCN	C_2H_2	CH_2CN	CH_3OH	NH_2CH_3		C_8H				
CN	HCO	$CH_2D^+?$	CH_4	CH_3SH	$c\text{-}C_2H_4O$						
CO	HCO^+	$HCCN$	HC_3N	HC_3NH^+							
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO							
CP	HOC^+	$HNCO$	$HCOOH$	NH_2CHO							
CSi	H_2O	$HNCS$	H_2CHN	C_5N							
HCl	H_2S	$HOCO^+$	H_2C_2O								
KCl	HNC	H_2CO	H_2NCN								
NH	HNO	H_2CN	HNC_3								
NO	$MgCN$	H_2CS	SiH_4								
NS	$MgNC$	H_3O^+	H_2COH^+								
$NaCl$	N_2H^+	NH_3									
OH	N_2O	SiC_3									
PN	$NaCN$										
SO	OCS										
SO^+	SO_2										
SiN	$c\text{-}SiC_2$										
SiO	CO_2										
SiS	NH_2										
CS	H_3^+										
HF											

Note that observations suggest the presence of large PAHs and fullerenes in the interstellar gas (Tielens et al 1999, Föing & Ehrenfreund 1997).

decay by emitting UV photons. The cosmic ray induced UV radiation field is approximately 10^3 photons s^{-1} cm^{-2} with an energy of $\sim$10 eV (Prasad & Tarafdar 1983, Gredel et al 1989). The overall geometry of protostellar sources—including outflows, shock regions, and hot cores, as well as the filamentary and clumpy structure of interstellar clouds—strongly influence the general line-of-sight conditions and the strength of the UV radiation field. Therefore, only combined information from astronomical observations (infrared and radio), interferometry, laboratory spectroscopy, and supporting theoretical models allows us to understand the formation and distribution of organics in the dense ISM.

More than 50 years ago, diatomic molecules such as CH, CH$^+$, and CN were reported from visible absorption of diffuse clouds (Swings & Rosenfeld 1937, McKellar 1940, Douglas & Herzberg 1941). Much larger molecules are now expected to be present in the interstellar gas and on dust grains in such environments. Among the large organic molecules observed or suspected in diffuse clouds are PAHs, fullerenes, carbon-chains, diamonds, amorphous carbon (hydrogenated and bare), and complex kerogen-type aromatic networks. The formation and distribution of large molecules in the gas and solid state is far from being understood. In the envelopes of carbon-rich late-type stars, carbon is mostly locked in CO and C_2H_2. C_2H_2 molecules are precursors for soot formation, where PAHs might act as intermediates (Frenklach & Feigelson 1989). The ubiquitous presence of aromatic structures in the ISM and in external galaxies has been well documented by numerous observations with the Infrared Space Observatory, or ISO (see special issue of *Astron. Astrophys.* 315, 1996). Evidence for carbon-chains and fullerenes arises from the characterization of the Diffuse Interstellar Bands (DIBs) (Freivogel et al 1994, Tulej et al 1998, Foing & Ehrenfreund 1994, 1997). Diamonds were recently proposed to be the carriers of the 3.4 and 3.5 μm emission bands (Guillois et al 1999) observed in planetary nebulae. Hydrogenated amorphous carbon (HAC) seems to be responsible for the 2200 Å bump in the interstellar extinction curve (Mennella et al 1998). A variety of complex aromatic networks are likely to be present on carbonaceous grains (Henning & Salama 1998).

The cosmic carbon abundance is an important criterion when considering the inventory of organics in the universe. Although the determination of solar carbon values indicates 355 ± 50 atoms per 10^6 H atoms (ppm) (Grevesse & Noels 1993), recent measurements using the Goddard High Resolution Spectrograph (GHRS) on the HST (Hubble Space Telescope) indicate interstellar carbon abundances that are only 2/3 of solar values (Cardelli et al 1996). A total carbon abundance of 225 ± 50 ppm is currently adopted (Snow & Witt 1995). The mean gas phase abundance of carbon is estimated to be $\sim$140 $\pm$ 20 ppm and is stable among different lines of sight, indicating no significant exchange between the dust and gas (Cardelli et al 1996). These new results provide strong constraints on carbonaceous dust models.

Comets are an agglomerate of frozen gases, ices, and rocky debris, and are likely the most primitive bodies in the solar system (Whipple 1950a,b). Comets

were formed in the region of giant planets and beyond, from remnant planetesimals that were not assembled into planets. Such comet nuclei have been ejected out of the solar system by gravitational interactions. A large number of comets formed in the zone of the giant planets are stored in the so-called Oort cloud at ∼50,000 AU from the solar system. Comet nuclei that were formed in the trans-Neptunian region reside in the Edgewood-Kuiper belt (Jewitt et al 1998). When comets are perturbed and enter the solar system, the solar radiation heats the icy material and forms a gaseous cloud, the coma. During this sublimation process, "parent" volatiles can be subsequently photolysed and produce radicals and ions, the so-called "daughter" molecules. In 1986, an international fleet of spacecraft (Giotto, Vega 1, Vega 2, Suisei, Sakigake, and ICE) encountered comet 1/P Halley. In situ investigations showed that Halley contained a large amount of dust and organic material (Kissel & Krueger 1987). Recent observations of two exciting bright comets, Hyakutake and Hale-Bopp, allowed astronomers to identify more than 25 parent species and strongly improved our understanding of cometary outgassing (Mumma 1997; Biver et al 1997, 1999; Lis et al 1997; Crovisier & Bockelée-Morvan 1999; Irvine et al 2000; Bockelée-Morvan et al 2000). The composition of comets encodes information on their origin and can be used as a tracer for processes that were predominant in the protosolar nebula.

A large number of organic species has been identified in meteorites (Cronin & Chang 1993). Samples of carbonaceous meteorites are the only pristine extraterrestrial material that can currently be studied on Earth, until future cometary missions allow in situ measurements and sample returns. The isotopic composition of extraterrestrial matter—in particular, D-enrichments and the $^{13}C/^{12}C$ ratio—provide evidence that interstellar matter has been incorporated in meteoritic material (Kerridge 1999). Cometary and meteoritic impacts on Earth in the first 100 million years may have delivered large amounts of organic molecules (Chyba & Sagan 1992). The richness of extraterrestrial organics may have allowed a jump start to the development of life—a topic of great interest for the emerging field of astrobiology (see http://www.astrobiology.com/).

In the following sections we review the formation of organic molecules in various environments of molecular clouds, and compare and contrast this inventory with that of solar system material. In Section 2.1, we discuss the formation of organic molecules in dense clouds by gas phase and grain surface reactions. In Section 2.2, we describe our current knowledge on the formation, evolution, and distribution of organics in diffuse interstellar clouds, and the formation of complex organics in circumstellar environments. Data on cometary organics from space missions to comet Halley, along with recent remote sensing data of volatiles in the comae of comets Hale-Bopp and Hyakutake, are reviewed in Section 3. In Section 4 we discuss organics measured in carbonaceous meteorites. The link between organic molecules in dark clouds and in the solar system and their implications for the origin of life are described in Section 5.

2.   ORGANIC MOLECULES IN THE INTERSTELLAR MEDIUM

The ISM is composed mainly of three types of clouds: dark clouds ($A_V > 5$ mag), translucent clouds (1 mag $< A_V < 5$ mag), and diffuse clouds (visual extinction, $A_V \leq 1$ mag) (Spaans & Ehrenfreund 1999). Interstellar clouds are neither uniform nor dynamically quiescent on long timescales. They display "clumpy" structures, are continually evolving as new stars form, and are enriched by material ejected from dying stars that was formed during stellar nucleosynthesis. Observations of atoms and molecules in interstellar clouds have been previously examined by Winnewisser & Herbst (1993), and Herbst (1995).

2.1   Organic Molecules in Dense Clouds

Dense interstellar clouds are the birth sites of stars of all masses and their planetary systems. Interstellar molecules and dust become the building blocks for protostellar disks, from which planets, comets, asteroids, and other macroscopic bodies eventually form (Weaver & Danly 1989, Levy & Lunine 1993, Mannings et al 2000). Observations at infrared, radio, millimeter, and submillimeter frequencies show that a large variety of gas phase organic molecules are present in the dense interstellar medium (Irvine et al 1987, Ohishi & Kaifu 1998, Winnewisser & Kramer 1999). These include organic classes such as nitriles, aldehydes, alcohols, acids, ethers, ketones, amines, and amides, as well as many long-chain hydrocarbon compounds. Such species display large compositional variations between quiescent dark clouds and star-forming regions, as well as strong abundance gradients on small spatial scales within each type of cloud (Irvine et al 1987, Olano et al 1988, van Dishoeck et al 1993, van Dishoeck & Blake 1998).

In the following sections we describe the solid state and gas phase inventories of molecular clouds, as revealed by ground-based and space-based observations. Table 2 summarizes the most abundant species observed in different regions of dense clouds and in the comae of bright comets, and lists their abundances relative to H_2O.

2.1.1 Organic Molecules Formed on the Grain Surface

The dust particles present in cold molecular clouds are important chemical catalysts. They can acquire icy grain mantles through the efficient but slow (typically one per day) accretion and reaction of atoms and molecules from the gas (Greenberg 1986, Whittet 1993, Schutte 1996, Tielens & Whittet 1997, Tielens & Charnley 1997). At low gas temperatures, sticking coefficients are generally expected to be close to unity for heavy atoms and molecules (Schmitt 1994), and their efficient removal from the gas phase occurs on the depletion timescale of $\tau \sim 3 \times 10^9/n_H$ yr, where n_H is the hydrogen nucleon number density. For $n_H > 10^4 \, \text{cm}^{-3}$, $\tau < 10^6$ yr, which is less than the expected lifetime of a dense core (Blitz 1993); therefore, regulatory mechanisms such as selective desorption

and mantle explosion are needed to maintain organic molecules in the gas phase (Léger et al 1985, Schutte & Greenberg 1991, Schmitt 1994, Willacy & Millar 1998).

An active chemistry takes place on grain surfaces that, in principle, can produce many complex interstellar molecules. At 10 K only H, D, C, O, and N atoms have sufficient mobility to scan the grain surface (by quantum tunneling or thermal hopping) and find a reaction partner (Tielens & Hagen 1982). Formation of the simplest mantle molecules (H_2O, NH_3, CH_4, etc.) can be explained by elementary exothermic hydrogen addition reactions, which do not possess activation-energy barriers (Allen & Robinson 1977, d'Hendecourt et al 1985, Brown & Charnley 1990, Hasegawa et al 1992). However, the presence of complex molecules such as CH_3OH and various unidentified organics indicates that other reaction processes also operate on and in the ice mantles. Although grain surface reactions of many neutrals, such as CO, possess activation barriers, H and D atoms can penetrate them by quantum tunneling, and can open up bonds for subsequent activation-less atom additions (Tielens & Hagen 1982). As dust grains with these simple ice mantles are transported from a cold quiescent phase to warm, dense, and active protostellar regions, other processes (such as ultraviolet irradiation, cosmic ray bombardment, and temperature variations) may become important and alter the grain mantle composition. Laboratory experiments show that irradiation processes of ice analogs lead to the formation of radicals, complex molecules, and even organic refractory material (Allamandola et al 1997, Moore & Hudson 1998, Kaiser & Roessler 1998, Greenberg 1999). Therefore, grain chemistry may become even more complex in high-energy environments.

Icy grain mantles have been recently studied with the Short Wavelength Spectrometer (SWS) on-board ISO. Observations of interstellar ices prior to ISO have been extensively reviewed by Whittet (1993) and Schutte (1996). In Figure 1 we display the spectrum toward the massive protostar W33A (Gibb et al 2000, Langer et al 2000). ISO allowed us for the first time observations of the complete range between 2.5 and 200 μm, free of any telluric contamination. The most recent abundances of interstellar ices near high-mass, low-mass, and field stars are listed in Table 2. H_2O is the major component of interstellar grains, but many features observed in the near- and mid-infrared are of organic nature. ISO-SWS and ground-based data show that the major organic species in interstellar ices are CO, CO_2, and CH_3OH (Table 2; Whittet et al 1996, Chiar et al 1998a, Dartois et al 1999b, Gerakines et al 1999). Organic species such as OCS, H_2CO, HCOOH, CH_4, and OCN^- are observed toward massive protostars and are characterized by abundances of a few percent relative to water ice (Whittet et al 1996, d'Hendecourt et al 1996, Schutte & Greenberg 1997, Ehrenfreund et al 1997a, Gibb et al 2000). Upper limits have been determined from ISO spectra for C_2H_2, C_2H_5OH, and C_2H_6 (Boudin et al 1998).

The stretching mode of CO is widely observed toward high- and low-mass protostars as well as in the quiescent medium (Tielens et al 1991, Chiar et al 1995, 1998a). The existence of hydrogen-rich ices (polar ices) and hydrogen-poor ices

TABLE 2 Millennium abundances of molecules in interstellar gas and ice and cometary volatiles

Molecule	W33A high	NGC7538 IRS9/high	Elias29 low	Elias16 field	Orion hot core	Comet Halley	Comet Hyakutake	Comet Hale-Bopp
H_2O	100	100	100	100	>100	100	100	100
CO	9	16	5.6	25	1000	15	6–30	20
CO_2	14	20	22	15	2–10	3	2–4	6–20
CH_4	2	2	<1.6	—	—	0.2–1.2	0.7	0.6
CH_3OH	22	5	<4	<3.4	2	1–1.7	2	2
H_2CO	1.7–7	5	—	—	0.1–1	0–5	0.2–1	1
OCS	0.3	0.05	<0.08	—	0.5	—	0.1	0.5
NH_3	15	13	<9.2	<6	8	0.1–2	0.5	0.7–1.8
C_2H_6	—	<0.4	—	—	—	—	0.4	0.3
HCOOH	0.4–2	3	—	—	0.008	—	—	0.06
OCN^-	3	1	<0.24	<0.4	—	—	—	—
HCN	<3	—	—	—	4	0.1	0.1	0.25
HNC	—	—	—	—	0.02	—	0.01	0.04

HNCO	—	—	—	—	0.06	—	0.07	0.06–0.1
C_2H_2	—	—	—	—	3–10	—	0.5	0.1
CH_3CN	—	—	—	—	0.2	—	0.01	0.02
$HCOOCH_3$	—	—	—	—	0.1	—	—	0.06
HC_3N	—	—	—	—	0.04	—	—	0.02
NH_2CHO	—	—	—	—	0.002	—	—	0.01
H_2S	—	—	—	—	1	0.04	0.8	1.5
H_2CS	—	—	—	—	0.01	—	—	0.02
SO	—	—	—	—	0.5	—	—	0.2–0.8
SO_2	—	—	—	—	0.6	—	—	0.1

Abundances are normalized to H_2O for interstellar ices and volatiles in comets Halley (1P/Halley), Hyakutake, (C/1996 B2) and Hale-Bopp (C/1995 O1). Abundances for the Orion hot core are normalized to CO. Recent ISO-SWS observations have allowed the ice abundances to be determined in the high-mass protostellar objects W33A (Gibb et al 2000, Keane et al 2000), NGC7538:IRS9 (Whittet et al 1996, Schutte 1999, Ehrenfreund & Schutte 2000a, Keane et al 2000), in the low-mass protostellar object Elias 29 (Boogert et al, Ehrenfreund & Schutte 2000a), and the field star Elias 16 (Whittet et al 1998, Schutte 1999). For W33A, the range given for each of HCOOH and H_2CO reflects the uncertainty in the H_2O ice column density (Gibb et al 2000, Keane et al 2000). Note that Keane et al(2000) recently estimated the values for NH_3 in the protostars W33A and NGC7538 to be below 9% relative to H_2O. Data for the Orion hot core are taken from vanDishoeck & Blake (1998) and Irvine et al (1999). Measurements for cometary volatiles are compiled from Crovisier & Bockelée-Morvan (1999), Mumma et al (1993), and Rodgers (1998). Molecules observed in comets, such as CO, H_2CO, HNC, OCS, and SO may have extended sources. For detailed information on the observations of individual species, the reader is referred to van Dishoeck & Blake (1998), Ehrenfreund & Schutte (2000a), Irvine et al (1999), Crovisier & Bockelée-Morvan (1999) and Cottin et al (1999).
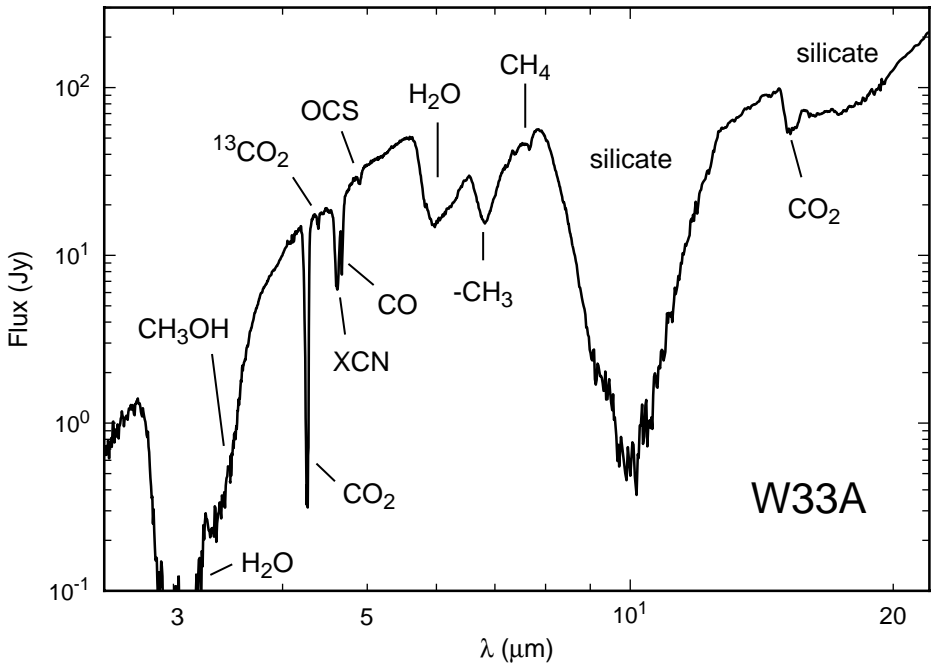
Figure 1   The ISO-SWS spectrum toward the protostar W33A (taken from Gibb et al 2000, Langer et al 2000). This cold and dense line of sight is characterized by large column densities of interstellar ices. Dominant absorption bands are visible at 3.0 μm (H_2O ice), 4.27 μm (CO_2 ice), 4.67 μm (CO ice), and 10 μm (silicates). The spectrum between 2 and 25 μm shows several additional species, many of them organic in nature.

(apolar ices) has been inferred from the CO band profile with the help of laboratory spectra (Sandford et al 1988, Tielens et al 1991). Polar ices, dominated by H_2O ice, in general evaporate around 90 K under astrophysical conditions and can therefore survive in higher-temperature regions close to the star (Tielens & Whittet 1997). Apolar ices, composed of molecules with high volatility (evaporation temperatures of <20 K) such as CO, O_2, and N_2 (Ehrenfreund et al 1998a), can only be formed and survive in cold, dense regions. During their passage through different cloud environments, grain mantles may accrete layers of polar and apolar ice.

The ubiquitous presence of CO_2 is one of the major discoveries of ISO. This molecule was observed through its stretching and bending vibrations at 4.27 and 15.2 μm, respectively (de Graauw et al 1996, d'Hendecourt et al 1996, Gürtler et al 1996, Whittet et al 1998, Gerakines et al 1999). Observations of $^{13}CO_2$ led to an estimate of the isotopic $^{13}C/^{12}C$ ratio in the galaxy (Boogert et al 2000). It has been shown that most of the CO_2 ice is present in annealed (hot) form on grain mantles and locked in intermolecular complexes with CH_3OH ice (Ehrenfreund

et al 1998b, Dartois et al 1999a,b). The formation of CO_2 in dense clouds in such large quantities ($\sim$20% relative to water ice; de Graauw et al 1996, Gerakines et al 1999) remains a mystery. It may be formed by grain surface reactions, namely by oxidation of CO. Energetic processing (UV irradiation or cosmic rays) or gas phase production in shocks and subsequent accretion on grains are alternative formation routes. Abundances of gaseous CO_2 are surprisingly low (van Dishoeck et al 1996, Dartois et al 1998), probably a result of destruction of CO_2 in shocks (Charnley & Kaufman 2000). Like CO_2, CH_3OH may be formed either by grain surface reactions (hydrogenation of CO; Hiraoka et al 1994) or by energetic processing. Recent ground-based observations indicate large amounts of CH_3OH in the line of sight toward some high massive protostars, but rather low CH_3OH ice abundances are observed toward low-mass protostars (Dartois et al 1999a). Recent ISO results also show extensive ice segregation of CO_2 and CH_3OH in the vicinity of protostars (Ehrenfreund et al 1998b, 1999a).

ISO gave the first high-quality observations of the strong 6.0 μm absorption band that is generally seen toward embedded protostars. Previously this band was ascribed to the deformation mode of H_2O. However, new data clearly showed excess absorption on the blue as well as the red wing of this feature (Schutte et al 1996, Keane et al 2000), which indicates the presence of the simplest organic acid, HCOOH (Schutte et al 1996), and of aromatic moieties (Schutte et al 1998), respectively. The presence of H_2CO, displaying a strong feature at 5.81 μm, is not yet confirmed, but a comparison with laboratory data indicates that H_2CO could be present in interstellar ices with an abundance of a few percent relative to water ice (d'Hendecourt et al 1996, Gibb et al 2000, Keane et al 2000). ISO was able to confirm the presence of CH_4 at 7.68 μm toward several objects, and showed an abundance relative to water ice of $\sim$2–4% (Boogert et al 1996, Dartois et al 1998). Gas phase abundances of CH_4 are generally lower than solid state abundances (Dartois et al 1998, van Dishoeck 1998, Boogert et al 1998). OCS is currently the only sulphur-containing species identified in interstellar ices, and shows an abundance of maximal 0.2% relative to water ice (Palumbo et al 1995, 1997; d'Hendecourt et al 1996). The tentative identification of the famous interstellar XCN band (Tegler et al 1995, Pendleton et al 1999) with OCN^- indicates that ions can be present and that acid-base reactions may occur on interstellar grain surfaces (Grim & Greenberg 1987, Schutte & Greenberg 1997, Demyk et al 1998). A further indication of more complex organic molecules present in interstellar ices is the weak absorption band at 3.25 μm detected in a number of massive YSOs (Brooke et al 1999, Sellgren et al 1994), which is currently assigned to the CH stretching mode of frozen PAHs. The presence of diamonds in dense clouds has been proposed by Allamandola et al (1992). Figure 2 shows a schematic outline of processes that can lead to the chemical diversity of interstellar ices and the formation of complex molecules in ice and gas (Ehrenfreund & Schutte 2000a).

No theoretical studies have examined detailed chemical reactions that occur by energetic processing, though much work has been done on modeling the molecular

THE CYCLE OF ICE AND GAS IN DENSE CLOUDS
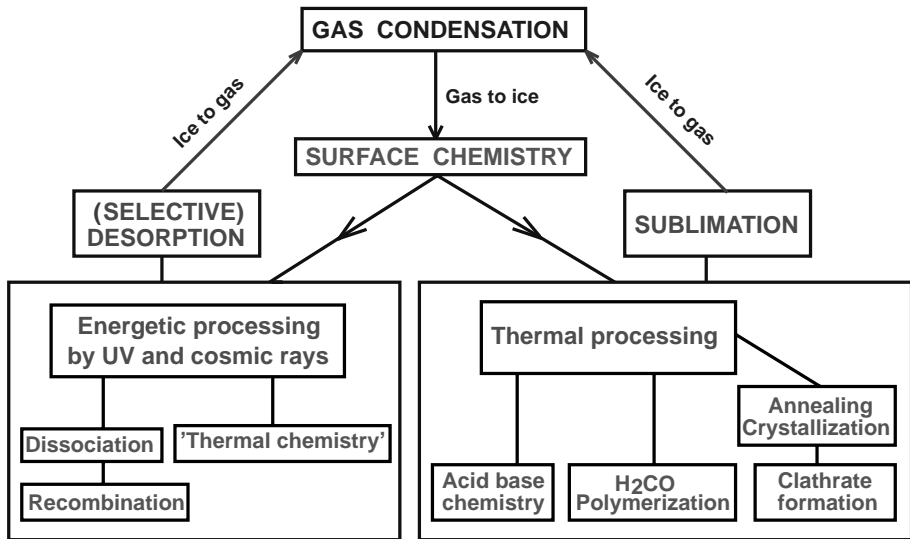
Figure 2 This diagram shows the cycle of gas and dust in dense clouds and the processes that lead to the formation of large complex molecules (Ehrenfreund & Schutte 2000a). For a detailed understanding, we refer to Schutte et al (1993) (formaldehyde polymerization), Gerakines et al (1996), Bernstein et al (1995), Briggs et al (1992) (UV processing), Ehrenfreund et al (1999a) (clathrate formation), Moore & Hudson (1992, 1998), Palumbo et al (1999) (cosmic ray processing), Schutte et al (1999) (acid-base reactions), Léger et al (1985) (selective desorption), and Sandford & Allamandola (1993) (sublimation).

complexity that could arise from grain surface reactions (Allen & Robinson 1977, d'Hendecourt et al 1985, Brown 1990, Hasegawa et al 1992, Hasegawa & Herbst 1993, Caselli et al 1993). However, progress in this area has been slow because most models neglect the stochastic nature of surface reactions and treat the surface populations as continuous deterministic variables (Pickles & Williams 1977). Even very simple surface reaction networks give different and implausible results when treated deterministically as opposed to stochastically (Tielens & Charnley 1997). Complex molecule abundances derived from deterministic models are therefore suspect. Despite recent attempts to reconcile the two approaches (Caselli et al 1998, Shalabiea et al 1998), at the present time a full stochastic simulation of both gas and grain chemistries appears to be required (Charnley 1998, Herbst 2000). The low solid and gas phase abundances of molecular oxygen found respectively by ISO and SWAS (Vandenbussche et al 1999, Melnick 2000) place stringent constraints on the efficiency of even simple surface reactions such as the combination of two oxygen atoms. Further experimental and theoretical effort is clearly necessary for

understanding the chemistry that can occur on dust grains and in the ice mantles that cover them, both in cold clouds and in the energetic conditions of star-forming regions.

2.1.2 Organic Molecules in Cold Dark Clouds

Prior to the onset of star formation, dust grains effectively shield molecules from interstellar UV photons; however, cosmic rays can penetrate throughout and drive a rich ion-molecule chemistry, supplemented by neutral-neutral processes, in which many complex organic species may be produced (Herbst 1987, Prasad et al 1987, Millar et al 1997, Herbst & Leung 1989). These reactions, along with grain surface processes, account for the high observed D/H ratios in interstellar molecules (Tielens 1983, Millar et al 1989).

The dark cloud TMC-1 contains a distinctive suite of many unsaturated carbon chain molecules (Ohishi & Kaifu 1998). These include the cyanopolyynes ($HC_{2n+1}N$, $n = 1 - 5$), various cumulene carbenes (H_2C_n, $n = 3, 4, 6$), and chain radicals (HC_n, $n = 1-8$); C_nN, $n = 1, 3, 5$), as well as some methylated molecules such as methylcyanoacetylene (CH_3CCCN) and methyldiacetylene (CH_3CCCCH). Various small molecules (CCO, CCCO, CCS, CCCS) are observed; their higher homologues and new homologous series may also be present (McCarthy et al 1997, Langer et al 1997, Guélin et al 1997, 1998; Thaddeus et al 1998, Bell et al 1999). Curiously, these organic molecules show spatial abundance gradients—they have their peak emission in a region of the cloud, the so-called "cyanopolyyne peak," which is physically distinct from other emission peaks in ammonia and DCO^+ (Gúelin et al 1982, Olano et al 1988, Pratap et al 1997). The challenge of the organic chemistry of TMC-1 involves both identifying the formation routes and explaining the spatial abundance gradients; most studies have concentrated on the former.

Early attempts at modeling the TMC-1 chemistry were based on ion-molecule pathways (Huntress & Mitchell 1979, Leung et al 1984, Millar & Freeman 1984, Millar & Nejad 1985, Millar et al 1987, Herbst & Leung 1989). It was subsequently realized that, for HC_3N, production in the neutral process involving CN and C_2H_2 could be important (Herbst & Leung 1990). Cherchneff & Glassgold (1993) showed that neutral-neutral reactions involving higher cyanopolyynes and polyacetylenes could consistently explain the abundances of these compounds in the carbon-rich envelope of the red giant IRC+10216. However, inclusion of these processes in models of interstellar chemistry tended to inhibit the production of complex species, primarily because of the high abundances of O, N, and C atoms present (Herbst et al 1994, Bettens et al 1995). Support for cold phase organic synthesis by neutral-neutral reactions comes from their rapid low-temperature rates (Sims et al 1993, Chastaing et al 1998), the fact that many of them are exothermic and have no energy barriers (Fukuzawa et al 1998), and the fact that observations of various ^{13}C isotopomers in TMC-1 confirm production of HC_3N by the reaction of CN with acetylene (Takano et al 1998).

Simple chemical models of TMC-1 predict that the gas phase organics should peak at very early times ($\sim 10^5$ years), when atomic carbon is abundant. This has led to the view that the various emission peaks in the ridge are at different evolutionary states, with the "cyanopolyyne peak" being the youngest (Hirahara et al 1992). Alternatively, Ruffle et al (1997) have shown that after an accretion time ($\sim 10^6$ years) organic abundances can peak as a result of the more rapid loss of destructive oxygen atoms; however, the predicted large depletions of CO and $N_2(N_2H^+)$ are not seen in TMC-1.

The fact that a few oxygen-bearing grain mantle molecules (see Section 2.1.1) are present at the "cyanopolyyne peak" led Markwick et al (2000) to construct a model of a transient gas phase chemistry where magneto-hydrodynamic waves from the embedded IRAS source induce grain-grain streaming, which leads to mantle explosions. Here, the "cyanopolyyne peak" chemistry is driven by acetylene molecules, which were formed and accreted earlier in the evolution of the ridge gas; the calculated abundance gradients along the ridge agree well with those determined by Pratap et al (1997).

In conclusion, it appears that neutral-neutral reactions are important for the production of many observed carbon chain molecules. The discovery and mapping of more cold sources similar to TMC-1 would allow further testing of this scenario.

2.1.3 Organic Molecules in Hot Molecular Cores

Star formation has a profound effect on the chemistry of the surrounding medium (van Dishoeck & Blake 1998, Wyrowski et al 1999, Langer et al 2000, van Dishoeck & van der Tak 2000). In the early phases of protostellar evolution, the surrounding gas and dust experience radiative heating and shock waves. Hot molecular cores are regions where evaporation and sputtering of icy grain mantles has recently occurred (Millar & Hatchell 1998); gas phase observations of these cores allows ice mantle composition to be probed to lower abundance levels than is possible by IR absorption spectroscopy. Hot cores are particularly rich in complex organic molecules and are typified by large abundances of water and ammonia (see Table 2) and enhanced deuterium fractionation ratios (e.g. Blake et al 1987, van Dishoeck et al 1993, Sutton et al 1995, Tielens & Charnley 1997, Irvine et al 2000).

Molecules observed in hot cores can have three possible origins. First, cold gas phase chemistry, combined with accretion onto dust during core collapse, can account for the presence of CO, HCN, and acetylene (Lahuis & van Dishoeck 2000). Second, grain surface reactions produce simple saturated compounds such as water and ammonia (Brown et al 1988). Both of these processes, which occur in preexisting cold material, can also explain the high deuterium fractionation ratios observed in specific molecules, such as HDO, NH_2D, DCN, D_2CO, and CH_2DOH (Tielens 1983, Brown & Millar 1989, Turner 1990, Jacq et al 1993, Millar et al 1995, Charnley et al 1997). For some time it was accepted that many of the complex organic molecules must be the products of grain surface chemistry. However, some

cores appear to be dominated by nitrogen-bearing molecules, and other adjacent ones by oxygen-bearing organic species (Blake et al 1987, Wyrowksi et al 1999). This can be explained by the third mechanism for producing hot core molecules: Evaporation of simple molecular mantles drives gas phase complexity (Charnley et al 1992). In this picture, the gas phase chemical differentiation results from small compositional differences between the ejected mantles; models have been proposed as to how this could occur (Caselli et al 1993).

Chemical models of hot cores can be used to identify molecules for which grain-surface production is necessary—e.g. ethanol, ketene, acetaldehyde, propynal, isocyanic acid, and formamide. This points to a surface chemistry seeded by CO molecules (Tielens & Hagen 1982). Hydrogen atom addition to CO leads to HCO (Hiraoka et al 1994, 1998), and subsequent H, C, N, and O atom additions lead to formaldehyde, ketene, isocyanic acid, and formic acid. These molecules can be further processed; for example, acetaldehyde and ethanol may be produced by consecutive hydrogen additions to ketene (Charnley 1997). When they are protonated, mantle-formed molecules such as methanol and ethanol (and perhaps higher alcohols) offer a very specific route to molecular complexity in hot cores through alkyl cation transfer to a neutral base, $R'X$,

$$ROH_2^+ + R'X \longrightarrow R'XR^+ + H_2O.$$
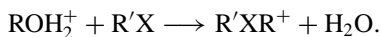
A large neutral organic molecule then results upon dissociative recombination with an electron. These reactions have been extensively studied in the laboratory (Mautner & Karpas 1986, Karpas & Mautner 1989). Evaporation of ices rich in methanol and ethanol should produce various pure and mixed ethers (Charnley et al 1995). The observed correlation of their distributions in star-forming regions (Minh et al 1993, Ikeda 1998) supports the view that dimethyl ether originates from the self-methylation of methanol. Figure 3 shows that several molecules could also be formed in this way and could predict the presence of many new, potentially detectable ones. Kuan et al (1999) have recently reported the tentative detection of diethyl ether. Recent calculations (Charnley & Rodgers 2000) suggest that evaporating ice mantles containing ammonia, as well as methanol and ethanol, could be the origin of the nitrogen-bearing organics (including CH_3CH_2CN, CH_2CHCN, CH_3CN, CH_3NH_2) that are seen in star-forming regions (Miao et al 1995, MacDonald et al 1996, Kuan et al 1996).

Future millimeter and submillimeter interferometers (cf. Bally et al 1995) such as ALMA will lead to the detection of complex molecules in protostellar cores with abundances almost a factor of a hundred below current detection limits. An exciting recent development is the demonstrated ability to detect simple organic species (e.g. HCN, HNC, CCH, H_2CO, CH_3OH) in the disks around low-mass stars (Dutrey et al 1997, Goldsmith et al 1999). Hence, an entire interstellar organic chemistry, including perhaps amino acids and other prebiotic molecules (Snyder 1997), may await discovery in objects that are prototypical of our own protosolar nebula.
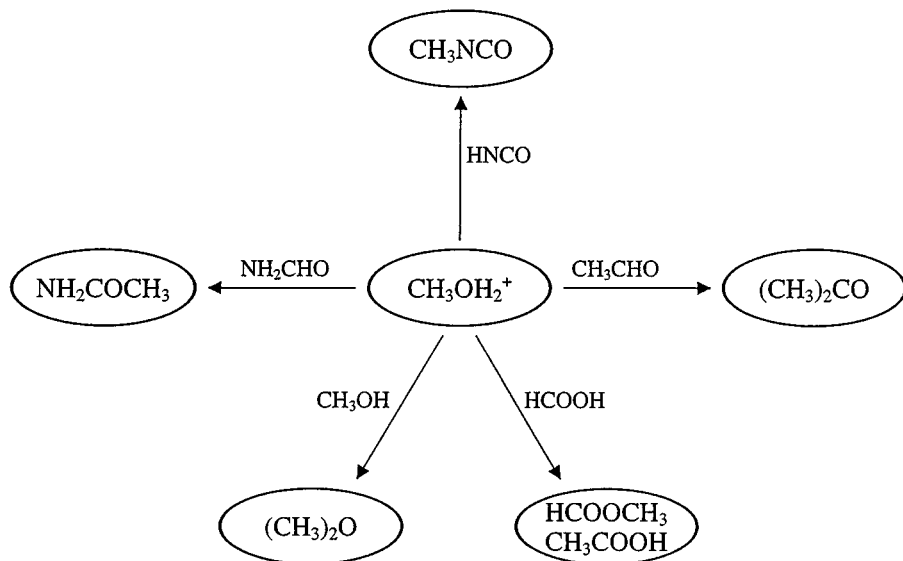
Figure 3   Methanol, when protonated, can transfer an alkyl cation to other evaporated neutral mantle products. In this figure, the step involving the electron dissociative recombination of the intermediate organic molecular ion has been suppressed for clarity.

2.2   Organic Molecules in the Diffuse Interstellar Medium

Diffuse clouds have moderate extinctions (<1 mag) and densities of roughly 100–300 cm^{-3}. They are characterized by an average temperature of ~ 100 K and a UV radiation field of approximately $\sim 10^8$ photons cm^{-2} s^{-1} (Mathis et al 1983). Since the initial discovery of simple diatomic molecules in interstellar space, CH, CN and CH^+ (Swings & Rosenfeld 1937, McKellar 1940, Douglas & Herzberg 1941), many more molecules have been detected in the photon-dominated diffuse medium, although at lower abundances than found in dense clouds. Species detected include: HCO^+, CO, OH, C_2, HCN, HNC, CN, CS and H_2CO (Lucas & Liszt 1997). Lucas & Liszt (2000) have recently detected C_2H and c-C_3H_2 in several extragalactic diffuse clouds and obtained upper limits on the column densities of l-C_3H and C_4H. The C_2H abundance varies little from diffuse to dense clouds whereas the c-C_3H_2 abundance is markedly higher in dense clouds. Reactions of the neutral molecules CH and CH_2 with C^+ can lead to the formation and build-up of polyatomic hydrocarbons. However, the presence of large carbon-bearing species is strongly dependent on their formation and survival rate because the diffuse medium is controlled by photochemistry. The larger carbonaceous molecules that enter the diffuse interstellar gas are detected in circumstellar envelopes around late-type stars (see Section 2.2.2). Evidence for carbonaceous dust particles is given by spectroscopy, polarization measurements, and theoretical models (Henning & Schnaiter 1999, Henning & Salama 1998).

About 1% per mass of the interstellar medium is in the form of solid dust grains, which may be carbon or silicon-based. Dust grains act as catalytic surfaces throughout the interstellar medium, and in general show dimensions on the submicron scale. The starlight is absorbed and scattered by dust grains and reaches the observer dimmed, a process referred to as extinction. The extinction-curve of the interstellar medium represents a superposition of the wavelength-dependent extinction properties of different dust particles. Different dust components that contribute to the line of sight extinction-curve are discussed by Dorschner & Henning (1995), Jenniskens & Greenberg (1993), Li & Greenberg (1997), and Vaidya & Gupta (1999). Dust particles in diffuse clouds and circumstellar envelopes can be composed of silicates, amorphous carbon (AC), hydrogenated amorphous carbon (HAC), diamonds, organic refractories, and carbonaceous networks such as coal, soot, graphite, quenched-carbonaceous condensates (QCC), and others. The dust size distribution could be inferred from astronomical observations in the UV, VIS, and IR (Mathis et al 1977, Dwek et al 1997). A three-component model of interstellar dust proposed by Desert et al (1990) suggests the coexistence of big grains (silicates with refractory mantles), very small grains (VSG, carbonaceous) and polycyclic aromatic hydrocarbons (PAHs). Li & Greenberg (1997) have modeled the interstellar extinction and polarization on the basis of a similar trimodal dust model, using the latest observational data and laboratory measurements.

Dust grains form in the cool expanding circumstellar environment of evolved stars (Sedlmayr 1994). Stellar winds inject dust into the ambient interstellar medium, which is then distributed by supernovae shock waves over large scales through the ISM. During this period, dust particles cycle several times through dense and diffuse clouds, which allows efficient mixing and processing of interstellar dust (Greenberg 1986, Mathis 1990). UV irradiation and cosmic rays, together with processes such as grain-grain collisions, sputtering, and grain growth, alter and destroy dust in interstellar and circumstellar regions (Jones et al 1996). Therefore, grains probably retain only traces of their origin, as evidenced by the isotopically anomalous composition of presolar grains found in meteorites (Zinner 1998). The life cycle of dust and interstellar depletions was recently discussed by Tielens (1998). Recent observations suggest that the abundance of carbon in the interstellar medium is only two-thirds of its solar value (Snow & Witt 1995, 1996; Cardelli et al 1996). This poses problems for many recent dust models, because only a limited amount of carbon is available for the dust phase (Snow & Witt 1995, Henning & Schnaiter 1999). In order to solve the so-called interstellar carbon crisis, Mathis (1996) proposed fluffy grain structures. Other solutions for the carbon abundance problem are discussed by Dwek (1997).

Organic molecules present in the diffuse medium can originate in one of three ways: (1) via gas phase reactions where model calculations of dispersing clouds allow the formation of molecules up to 64 C atoms with ion-molecule reactions and neutral-neutral reactions (Bettens & Herbst 1996); among them are unsaturated C-chains, single- and triple-ring structures, and fullerenes (Herbst 1995, Ruffle et al 1999); (2) by reactions in circumstellar envelopes and subsequent mixing into the diffuse medium (only very photoresistant species; see Section 2.2.2); and

(3) from carbonaceous dust by photochemical reactions and grain collisions. Grain surface reactions have also been suggested, but these are only expected to produce simple hydrides (e.g. NH; Wagenblast et al 1993).

2.2.1 Spectroscopic Evidence for Carbonaceous Compounds in the DISM

A large and diverse suite of organic compounds is believed to reside and evolve in the diffuse medium (Papoular et al 1996, Henning & Salama 1998). In this section we first list the main spectroscopic features observed in diffuse clouds, the carriers of which remain unknown, but are likely of a carbonaceous nature. The spectroscopic puzzles in the ultraviolet, optical, and infrared range are the ultraviolet bump at 2200 Å, the diffuse interstellar bands (DIBs), the extended red emission (ERE), the 3.4 μm absorption, and the infrared emission features between 3 and 15 μm (UIR). We then discuss the most important organic species such as PAHs, fullerenes, and diamonds, as well as solid organic compounds possibly present in the DISM.

The UV Bump at 2200 Å   By far the strongest feature in the interstellar extinction curve is the ultraviolet bump at 2200 Å. It is characterized by a stable position, but its band width changes according to the interstellar environment (Fitzpatrick & Massa 1986). The carrier of the ultraviolet bump has not yet been identified. Among the numerous proposed candidates are graphite grains (Stecher & Donn 1965, Annestad 1992), graphitic onions (Wright 1988), hydrogenated amorphous carbon (HAC) (Mennella et al 1996), core particles (made of silicates or graphite) with a mantle of PAHs (Mathis 1994, Duley & Seahra 1998), and coal-like material (Papoular et al 1996). An important contribution of a mixture of PAHs to the UV bump has been proposed by Joblin et al (1992). Molecular aggregates with aromatic double-ring structures produced in plasma discharge are discussed by Beegle et al (1997). Recent theoretical calculations and laboratory data propose onion particles as possible carriers (Henrard et al 1997, Wada et al 1999). Isolated nanometer-sized C particles show a UV bump as narrow as the interstellar feature and a good fit in wavelength position (Schnaiter et al 1998). Mennella et al (1998) attribute the UV bump to a population of nano-sized, UV-processed hydrogenated amorphous carbon grains. The latter authors propose a class of material whose optical properties vary according to the processing degree in different regions of the interstellar medium. All recent results point strongly toward a carbonaceous carrier for the UV bump.

The Diffuse Interstellar Bands (DIBs) between 4000 and 10,000 Å   The Diffuse Interstellar Bands (DIBs) are absorption lines detected in the spectra of nearby stars. They are observed in a spectral range extending from 0.4 to 1.3 μm and exhibit a strong diversity of profiles (Full Width at Half Maximum, or FWHM, ranging from 0.8 to 30 Å) (Herbig 1995). The detection of DIBs in almost all ISM regions
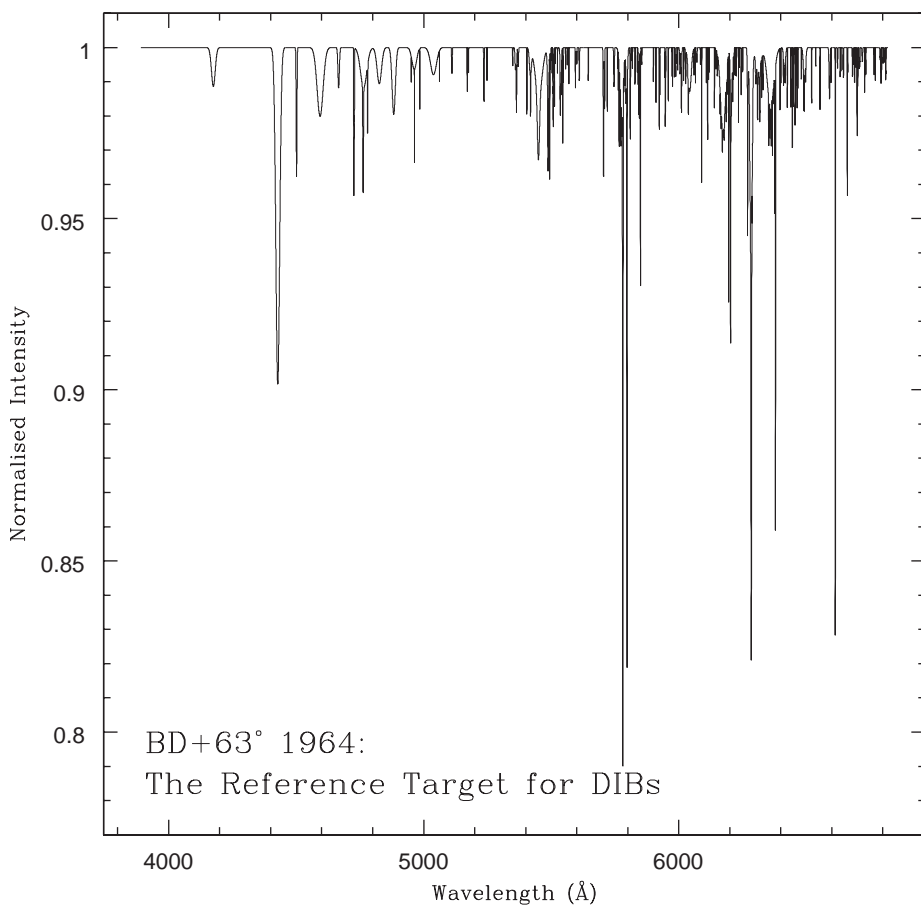
Figure 4   The synthetic spectrum of the hot B0II star BD+63 1964. This object, characterized by an $E_{(B-V)} = 1$, is currently used as a reference target of diffuse bands, displaying more than 250 DIBs in the range 3900–7000 Å and a significant enhancement of narrow DIBs (Ehrenfreund et al 1997b, O'Tuairisg et al 2000).

indicates chemically stable carriers. In the past 75 years, a number of surveys were initiated to constrain better the nature of the DIB carriers. The DIB number rose to around 200 in 1994 (Jenniskens & Desert 1994, Krelowski et al 1995). Presently, more than 250 DIBs are reported (O'Tuairisg et al 2000). Figure 4 shows the synthetic DIB spectrum of the hot star BD+63 1964 (Ehrenfreund et al 1997b, O'Tuairisg et al 2000).

As DIB strength correlates with reddening, dust grains and impurities embedded in dust particles have been among the proposed carriers in the past (Herbig

1995). However, the solid state theory did not explain the ubiquitous presence and the high wavelength stability of DIBs. The DIBs' strength is dependent on the environmental conditions (Herbig 1975, Snow et al 1995, Krelowski et al 1998). Observations show that the DIB strength progressively decreased in cloud interiors (Adamson et al 1991). This "skin effect" has recently found further support (Herbig 1993, Cami et al 1997, Sonnentrucker et al 1997).

Many results seem to point toward carrier molecules that are of gas phase origin, chemically stable, and carbonaceous in nature (Herbig 1995). Cami et al (1997) completed the first survey of DIB correlations over 4000 Å, which showed that most of the DIB carriers are undergoing photoionization and that all measured DIBs do originate from different carriers. The detection of DIBs in emission in the Red Rectangle (Scarrott et al 1992) and the detection of intrinsic substructures in the profile of several DIBs indicate the molecular nature of some DIB carriers (Sarre ET AL 1995, Ehrenfreund & Foing 1996, Krelowski & Schmidt 1997, Le Coupance et al1999).

Recent laboratory studies point toward PAHs, carbon chains, and carbon rings or fullerenes as potential carriers for some DIBs (Salama et al 1996, Freivogel et al 1994, Tulej et al 1998, Ehrenfreund & Foing 1996, Foing 1996, Foing & Ehrenfreund 1997). Theoretical models of large carbonaceous carrier molecules constrain the formation and destruction rate of such species in the diffuse medium (Allain et al 1996a,b, Bettens & Herbst 1997, Jochims et al 1999, Ruffle et al 1999). The search for specific bands of PAH cations in highly reddened stars shows some coincidences with small PAHs measured in the gas phase or in neon matrices (Salama et al 1999). In the near future, measurements using larger PAH molecules may show better agreement. Carbon chains measured in the gas phase show coincidences with the band position of some DIBs (Freivogel et al 1994). In particular, the anion C_7^- has been suggested as a potential DIB carrier (Tulej et al 1998). However, high-resolution astronomical data indicate that the band ratios for this species are variable in several stars (Galazutdinov et al 1999). Additionally, the abundance of carbon chains in the diffuse medium is estimated to be very low— 10^{-10} per H atom, a factor 1000 lower than the estimated PAH abundance. This strongly suggests a limited contribution of carbon chains to the DIB spectrum (Allamandola et al 1999a, Motylewski et al 2000). Foing & Ehrenfreund (1997) observed two DIBs at 9577 and 9632 Å as first evidence for C_{60}^+, the largest molecule ever detected in space. This conclusion was based on the laboratory spectrum of C_{60}^+, in a neon matrix obtained by Fulara et al (1993) and has to be confirmed by a comparison with the gas phase spectrum of the C_{60} cation.

At present, no definitive identification of the carriers of more than 250 bands exists. For a correct identification of the DIB carriers, gas phase spectroscopy is an important tool of the present and future (Freivogel et al 1994, Tulej et al 1998, Brechignac & Pino 1999, Romanini et al 1999). The complexity of interstellar processes, the wealth of DIBs and potential carriers, and technical limitations may account for the lack of success in the past. Attempts were made to correlate the DIB strength variations with extinction curve parameters, grain properties,

the interstellar radiation field, and other interstellar atoms and molecules (Herbig 1993, Adamson et al 1991, Krelowski et al 1995, Desert et al 1995, Krelowski et al 1999, Sonnentrucker et al 1999). Although constraints could be evaluated for a few DIBs, a consistent picture remains elusive (Snow 1997). The recent search for DIBs in the solar system, namely in the coma of Hale-Bopp, was not successful (Herbig & McNally 1999). The identification of the DIB carriers will remain an important problem in astronomy in the new millennium.

The Extended Red Emission (ERE)   The extended red emission has been detected in many dusty astrophysical objects and appears to be a general characteristic of dust (Gordon et al 1998). ERE is a broad, structureless emission band that appears between 5400–9400 Å and is attributed to the photoluminescence of particular dust grains. The central wavelength of the ERE varies from object to object, and their spectral nature and photon conversion efficiency requires an abundant carrier in the ISM, such as carbon or silicon-based material (Witt et al 1998). The carbonaceous candidates proposed as carriers for the ERE are the same substances that have been proposed for the UV bump, namely HAC (Duley 1985), QCCs (Sakata et al 1992), coal (Papoular et al 1996), small carbon particles of mixed sp^2/sp^3 hybridized bonding (Seahra & Duley 1999), PAHs (d'Hendecourt et al 1986), and fullerenes (Webster 1993). The recent comparison of photoluminescence properties of carbon- and silicon-based material through observations indicates that the ERE carrier might be silicon-based (Witt et al 1998, Ledoux et al 1998). Zubko et al (1999) conclude that the intrinsic photon conversion efficiency of the photoluminescence by silicon nanoparticles must be near 100%, if they are the source of the ERE.

The 3.4 μm Feature of Aliphatic Hydrocarbons   The spectra of several sources located close to the Galactic center, and Wolf Rayet stars, show the signature of organic structures on grains at 3.4 μm (Pendleton et al 1994, Sandford et al 1991, 1995). This feature is attributed to the symmetric and asymmetric C–H stretching modes of aliphatic hydrocarbons. The detection of the 3.4 μm absorption toward the Seyfert galaxy NGC1068 (which has an active nucleus obscured by dust) and the IRAS galaxy 08572+3915 offers exciting future perspectives (Wright et al 1996). The strong consistency in spectral signatures in different galaxies suggests the preferential formation of a common carbonaceous structure. The 3.4 μm feature is also observed in infrared spectra of solar system material, such as captured interplanetary dust particles (IDPs) and organic extracts of the meteorites Orgueil and Murchison (Ehrenfreund et al 1991, Pendleton et al 1994; see also Figure 5). The C–H stretching mode of hydrocarbons is a rather unspecific feature that can arise in many different kinds of carbonaceous material. Therefore numerous fits of carbon-containing material have been proposed as identification of the 3.4 μm feature (see Pendleton et al 1994 for a review). It is generally assumed that the 3.4 μm band may result from aliphatic chains that act as bridges in a carbonaceous network (as is found in kerogens and coals), residing on interstellar grains.

A new 2.8–3.8 μm spectrum of the carbon-rich protoplanetary nebula CRL 618 (Chiar et al 1998b) confirms the previous detection of a circumstellar 3.4 μm absorption feature in this object (Lequeux & Jourdain de Muizon 1990). The observations imply that the carriers of the interstellar 3.4 μm feature are produced, at least in part, in the circumstellar environment by post-processing of carbon grains during the transition from the AGB to the planetary nebula phase (Chiar et al 1998b, Mennella et al 1999). This raises doubts as to whether this material is produced by the processing of interstellar ices in dense interstellar clouds, as was previously proposed (Greenberg et al 1995). Schnaiter et al (1999) tried to match the 3.4 μm profile of CRL618 with carbon particles condensed from carbon vapor in a hydrogen-rich quenching atmosphere. Mennella et al (1999) studied the interaction of atomic H with nano-sized carbon grains, the 3.4 μm feature produced in this way also fits the absorption band seen toward the Galactic center, as well as toward CRL618.

The absence of the 3.4 μm feature in AGB stars, the progenitor stars for CRL618 (Chiar et al 1998b), and in dense interstellar clouds (Allamandola et al 1992) may give clues to its origin. Recent laboratory studies of hydrocarbons covered with ice, simulating dense cloud conditions, suggest that the 3.4 μm band is not present, because in such an environment hydrocarbons are efficiently dehydrogenated through interaction with H_2O ice and UV photons (Munoz et al 2000). Spectropolarimetry of the 3.4 μm aliphatic C–H stretch feature, in the line of sight from the Galactic center source IRS 7, showed an unpolarized feature not associated with the aligned silicate component of interstellar dust (Adamson et al 1999). The simplest explanation is that the 3.4 μm carrier resides in a population of small, nonpolarizing carbonaceous grains, physically segregated from the silicates. To summarize, the current results indicate that a mechanism able to form C–H bonds must be active, and that carbon grains produced in carbon-rich AGB stars may be hydrogenated in the diffuse medium (Mennella et al 1999). Figure 5 shows a comparison of the 3.4 μm feature in an external galaxy, our Galactic center, and an extract of the Murchison meteorite (Pendleton 1997), which indicates that the formation process of such material is widespread in the Universe.

The Infrared Emission Bands between 3 and 15 μm   The infrared emission bands at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.7 μm are observed in the diffuse interstellar medium, in circumstellar environments, and even in external galaxies. These bands are attributed to the C–H stretching and bending vibrations and C=C stretching modes in aromatic molecules (Léger & Puget 1984, Allamandola et al 1987, Puget & Léger 1989). In previous years, many components have been proposed to be responsible for these features. Among them are PAHs, hydrogenated amorphous carbon (HAC), quenched carbonaceous composites (QCCs), and coal (see Tielens et al 1999 for a recent review). The ISO satellite has revisited the IR emission bands and showed their ubiquitous presence in our own as well as external galaxies (see special issue of *Astron. Astrophys.* 315, 1996). High-resolution infrared spectra of different interstellar environments display (apart from the main bands)
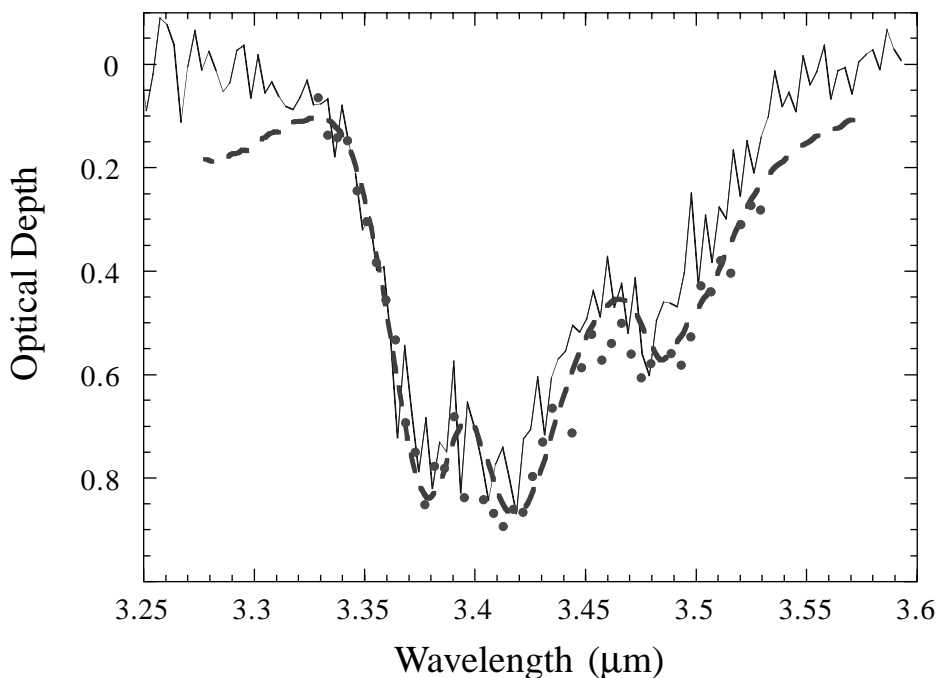
Figure 5   The 3.4 μm absorption signature of C–H stretching modes in aliphatic hydrocarbons is shown as observed toward the extragalactic source (IRAS 08572+3915) (*solid line*) and our Galactic center (IRS6) (*points*), and measured for an organic residue of the Murchison meteorite (*dashed line*) (taken from Pendleton 1997). The similarity of these spectra indicates pathways of carbon chemistry that are selected throughout the universe.

new additional weak features, shoulders, and subfeatures, as well as plateaus and a varying underlying continuum (Lemke et al 1998, Klein et al 1999, Tielens et al 1999). Figure 6 shows infrared spectra of various objects in the diffuse ISM. Observations of the infrared emission bands in cirrus clouds indicate the presence of PAHs in the gas phase. In such environments the radiation field is so low that there is no alternative mechanism to the transient heating of small particles by absorption of a single photon (Mattila et al 1996, Boulanger et al 1998). Modeling of the infrared dust bands by Lorentz profiles produced perfect fits to spectra obtained with ISO-CAM (on-board ISO). Those profiles indicate particles of a few hundred atoms (Boulanger et al 1998). Theoretical calculations of the relative emission strengths of neutral and ionized PAHs (Langhoff 1996) and laboratory studies have allowed the infrared emission bands to be successfully modeled by combining laboratory spectra of neutral and positively charged PAHs (Hudgins & Allamandola 1999a,b, Allamandola et al 1999b). The particle size of these fits indicates a PAH size distribution between 20 and 90 C atoms. Tielens et al (1999) argue for the presence of PAH with ~50 C atoms. Apparently there is not
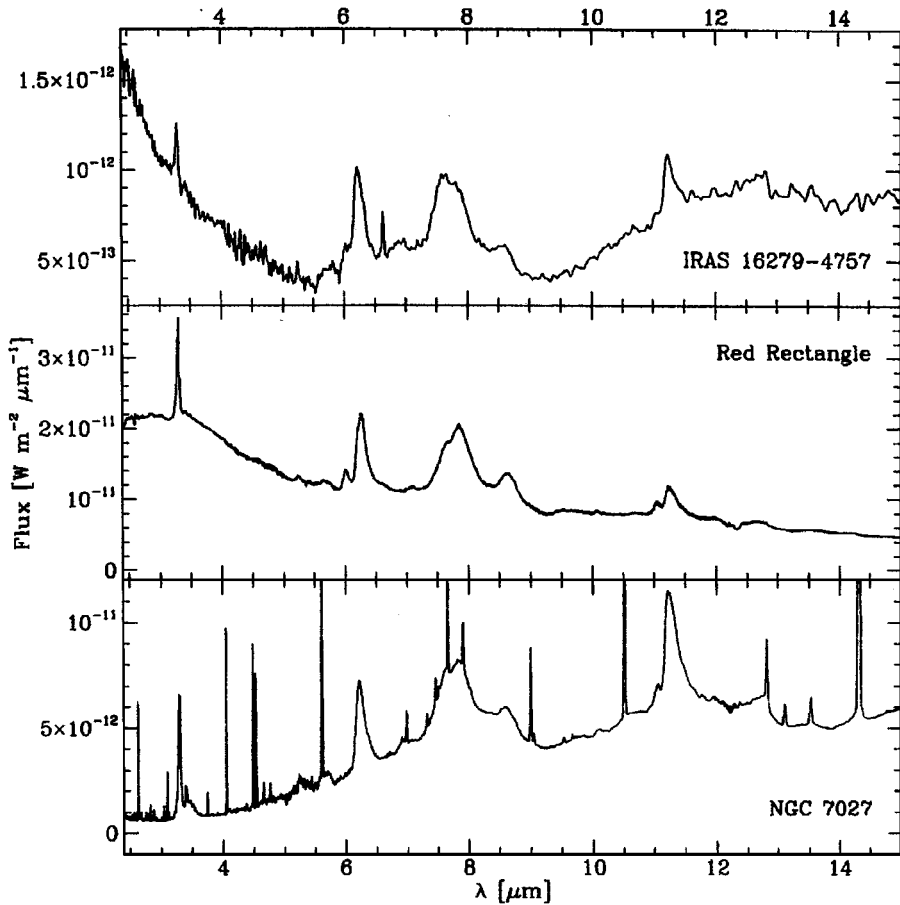
Figure 6   ISO-SWS 3–15 μm emission spectra of the post AGB objects, IRAS 16279-4757, the Red Rectangle, and the planetary nebula NGC 7027. The different objects display a rich and variable spectrum of infrared emission bands (taken from Tielens et al 1999).

yet a consensus on the PAH size distribution in the interstellar medium, but it is likely that free individual PAH molecules, PAH clusters, and particles composed of PAH subunits are responsible for the overall interstellar emission spectrum (Allamandola et al 1999b). The amount of cosmic carbon locked up in PAH molecules is a substantial fraction of ∼20% (Dwek et al 1997). ISO spectra showed new bands in the region between 10 and 15 μm, which may be attributed to phenyl groups, and a plateau between 16 and 20 μm, which is attributed to larger PAH clusters, including five-ring structures such as fluorathenes (van Kerckhoven et al 2000). PAHs might show strong diversity because of various attached side groups. Organometallic molecules formed by efficient reactions between aromatics and transition metals have been proposed by Serra et al (1992).

The observed 2–13 μm emission spectra of carbon-rich post-AGB stars, including both bands and continuum, could be well matched with the computed infrared emission spectra of semi-anthracite coal grains (Guillois et al 1996), which provides evidence for the presence of solid aromatic compounds (Papoular et al 1996). Although the nature of molecules responsible for the infrared emission bands is no doubt aromatic, the individual components will have to be identified in future laboratory experiments.

2.2.2 Organic Molecules in Circumstellar Envelopes

The massive circumstellar envelopes (CSEs) of late-type, post-AGB stars are pivotal to the evolution of the ISM because they provide the dust and refractory species for the diffuse medium, and yet require the existence of the dense medium to beget the stars. The bulk of the stardust originates in oxygen-rich M giants, radio-luminous OH/IR stars, supergiants, and carbon stars (e.g. Gail & Sedlmayr 1987). Grains are formed near the photosphere and drive the circumstellar wind. For stars with O/C<1, the carbon not in CO is primarily contained in acetylene and is available for incorporation into organic molecules, carbonaceous grains, and refractory molecules such as SiC (Blanco et al 1998, Mutschke et al. 1999). Carbon stars show strong PAH emission, and it has been proposed that PAH formation is the key step to the production of carbon dust (soot) (Frenklach & Feigelson 1989, Cherchneff et al 1992). Alternative chemical pathways to soot formation are based on neutral radicals, ions, C-chains, and fullerenes as intermediates (see Tielens & Charnley 1997). Pure carbon dust can exist only in hydrogen-deficient stars, therefore carbon-rich WR stars with envelopes of He, C, and O may be a source of interstellar fullerenes (Cherchneff & Tielens 1995). Recent ISO results showed that the chemical evolution of carbonaceous dust from aliphatic to aromatic structures can rapidly take place as the stars evolve (Kwok et al 1999).

In oxygen-rich CSEs, the available carbon is in CO and does not contribute to formation of grains, which are silicates. However, many objects show the anomalous presence of simple organic molecules such as HNC, HCN, CN, CS, and H_2CO (e.g. Omont 1993, Bujarrabal et al 1994). Several explanations have been advanced to explain these anomalies, but at present this problem is unresolved (Nejad & Millar 1988, Nercessian et al 1989, Beck et al 1992, Charnley & Latter 1997, Willacy & Millar 1997, Duari et al 1999). Interestingly, weak PAH emission in combination with silicate absorption has been found in the shells of several O-rich supergiants (Voors 1999, Voors et al 1999) and O-bearing molecules have been detected in carbon-rich proto-planetary nebulae (Herpin & Cernicharo 2000).

The carbon-rich envelope of IRC+10216 contains a large variety of organic molecules (Glassgold 1996) and is dominated by the presence of many carbon chain molecules, including polyacetylenes (e.g. C_8H; Cernicharo & Guélin 1996), cyanopolyynes (e.g. HC_9N; Bell et al 1992) and sulfuretted chains (CCS, CCCS, and possibly CCCCCS; Cernicharo et al 1987, Bell et al 1993). Structural isomerism has also been found in carbon chain molecules (e.g. HCCNC versus HC_3N;

Gensheimer 1997). Many of these molecules are also detected in the dark cloud TMC-1 (see Section 2.1.2). Molecular observations of IRC+10216 at IR and millimeter wavelengths have recently been reviewed by Cernicharo (2000) and Guélin (2000). In the outer regions of the envelope, outflowing gas is photodissociated and photoionized to produce ions and radicals. Neutral-neutral reactions are believed to be crucial to the formation of cyanopolyynes and polyacetylenes (Cherchneff & Glassgold 1993, Cherchneff et al 1993, Millar & Herbst 1994) as well as several organo-silicon compounds (Howe & Millar 1990, MacKay & Charnley 1999). Alternative explanations for the observed prevalence of carbon chains involve either direct disruption of carbonaceous grains by UV photons or grain collisions (Jura & Kroto 1990) or production on grain surfaces followed by UV photodesorption (Guélin et al 1993).

Red giant CSEs thus provide the bulk of the raw material for Galactic organic chemistry. Except for the most photochemically resilient species (PAHs, fullerenes, dust grains), molecules formed in the red giant CSEs are destroyed in the very outermost layers as they leave the circumstellar envelope and enter the diffuse ISM.

2.2.3 Evidence for Specific Organic Molecules

The current abundance estimates (per H atom) of large carbonaceous molecules contributing to the interstellar carbon budget are 10^{-7} for PAHs, 10^{-8} and 10^{-10} for carbon chains in dense and diffuse clouds, respectively, and 10^{-8} for fullerenes (Tielens et al 1999, Allamandola et al 1999a). A large amount of carbon (up to $\sim$50% of the total cosmic carbon) may be locked in carbonaceous solids (e.g. O'Donnell & Mathis 1997, Li & Greenberg 1997).

Polycyclic Aromatic Hydrocarbons (PAHs)   PAHs are believed to be the most abundant free organic molecules in space (Puget & Léger 1989, d'Hendecourt & Ehrenfreund 1997). Electron delocalization over their carbon skeleton makes them remarkably stable. As discussed in Section 2.2.2, PAH molecules are produced partly in the outer atmospheres of carbon stars or formed by shock fragmentation of carbonaceous solid material. PAHs may eventually also form in the diffuse interstellar gas by neutral-neutral reactions (Bettens & Herbst 1996) or by energetic processing of specific ices in dense clouds (Kaiser & Roessler 1998). PAHs play a central role in the gas phase chemistry (Bakes & Tielens 1994, 1998). The environmental conditions and the local ultraviolet radiation field determine their charge and hydrogenation state. Theoretical calculations imply that PAHs with <50 C atoms can be destroyed or fragmented in UV-dominated regions (Allain et al 1996a). In their evolutionary cycle, PAH molecules may freeze out onto grains in dense clouds, an idea that is supported by recent ISO observations toward M17 (Verstraete et al 1996). PAHs are ubiquitously distributed in the interstellar medium and are also seen in traces in solar system material (Clemett et al 1993). PAHs in the interstellar gas are likely responsible for the infrared emission bands and may contribute to the DIB spectrum.

Fullerenes   The polyhedral geometry of C_{60} was discussed for the first time by Kroto et al (1985). In 1990, C_{60} was efficiently synthesized in macroscopic quantities by Kraetschmer et al (1990). The presence of soot material in carbon-rich stars, along with the spontaneous formation and remarkable stability of the fullerene cage suggest the presence of fullerene compounds in interstellar space (see Ehrenfreund & Foing 1997 for a review). Fullerenes may be formed in small amounts in envelopes of R Coronae Borealis stars (Goeres & Sedlmayr 1992). Theoretical models show the possible formation of fullerenes in the diffuse interstellar gas via the buildup of C_2–C_{10} chains from C^+ insertion, ion-molecule reactions, and neutral-neutral reactions (Bettens & Herbst 1996, 1997). Recent fingerprints of the C_{60}^+ ion were discovered in the near-infrared, which indicate that fullerenes can play an important role in interstellar chemistry (see Section 2.2.1; Foing & Ehrenfreund 1994, 1997). The abundance of C_{60}^+ was inferred from optical measurements to be 0.3–0.9% of the cosmic carbon (Foing & Ehrenfreund 1997). The search for vibrational transitions (in the mid-IR) in emission of C_{60} and C_{60}^+ in the reflection nebula NGC 7023 was negative, and only uncertain upper limits could be determined (Moutou et al 1999). Garcia-Lario et al (1999) attribute the 21 μm dust feature observed in the C-rich protoplanetary nebula IRAS 16594-4656 to fullerenes, which may be formed during dust fragmentation. However, many different carrier species have been proposed for this broad strong emission band (e.g. Hill et al 1998). C_{60}^+ may be abundant in the ISM, as well as endo- and exohedral fullerene compounds (Kroto & Jura 1992). Interstellar hydrogenated fulleranes have been discussed by Webster (1995). Fullerenes—and in particular, higher fullerenes—have recently been detected in the meteorites (see Section 4; Becker & Bunch 1997, Becker et al 1999a). Fullerenes have also been detected in an impact crater on the LDEF spacecraft (di Brozzolo et al 1994).

Diamonds in Space   A main route of synthesis of diamonds in the interstellar medium could be the growth by chemical vapor deposition mechanism (CVD) in the expanding envelopes of Type II supernovae (Clayton et al 1995). But diamonds might also be formed in stellar environments by high velocity grain-grain collisions behind supernova shock waves (Tielens et al 1987, Blake et al 1988). Different methods for gas phase synthesis of nanodiamonds are discussed by Hahn (1997). The infrared band at 3.42 μm detected in the spectra of massive protostars falls near the position of C–H stretching vibrations in tertiary carbon atoms and suggests a carrier with a diamond-like structure (Allamandola et al 1992, 1993). Interstellar nanodiamonds have been proposed to be the carriers of the unidentified 21 μm infrared emission feature observed in the dust shells around some carbon-rich protoplanetary nebulae (Hill et al 1998). Small crystallites of diamonds have been recently identified in dusty envelopes by Guillois et al (1999), who attributed the two peculiar unidentified infrared emission bands at 3.43 and 3.53 μm to the vibrational modes of hydrogen-terminated crystalline facets of diamonds (see Figure 7). The intensities of these two features as measured in the Herbig Ae/Be star HD97048 correspond to a mass of 10^{-10}–10^{-9} solar masses of diamond dust
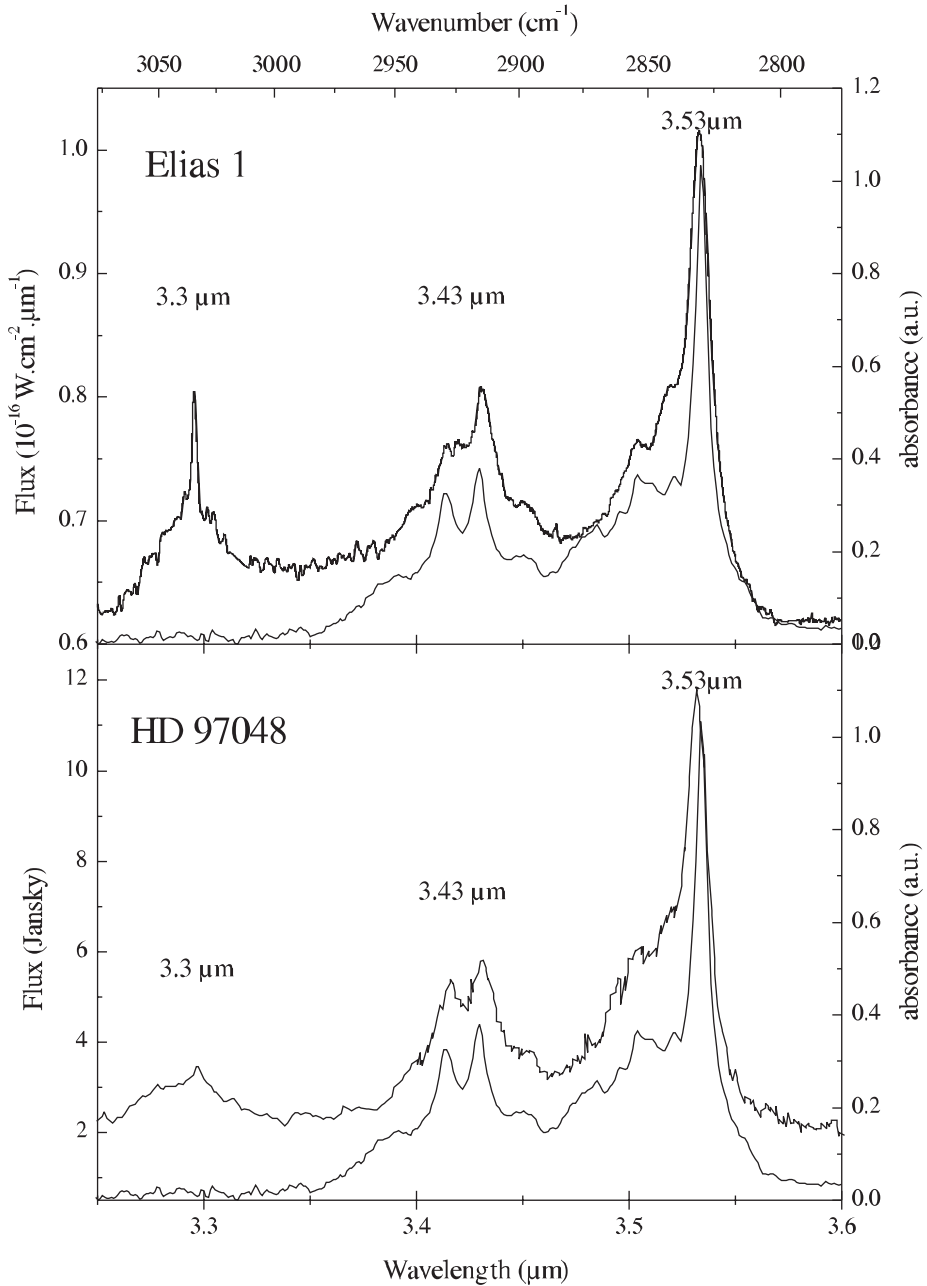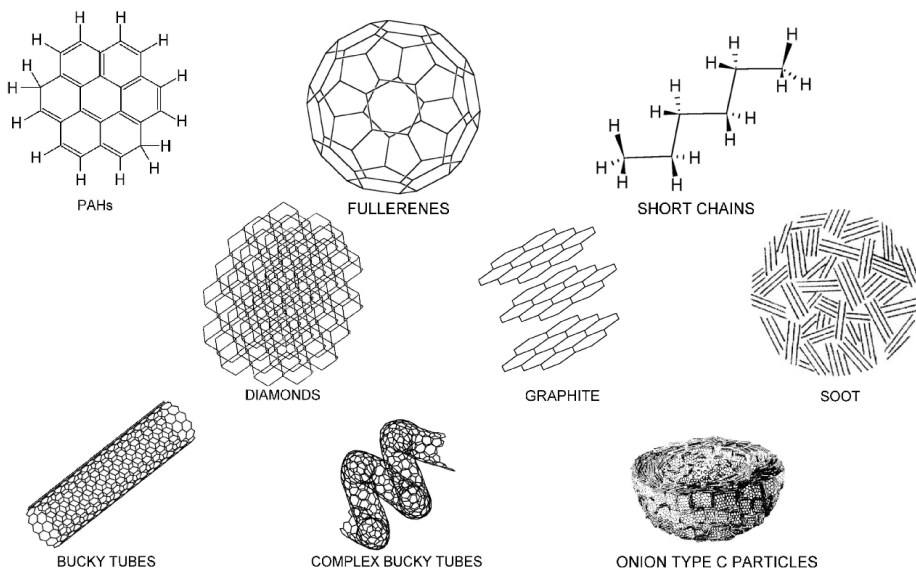
Figure 7 Spectroscopic comparison between the emission spectra of Elias 1 (top) and HD97048 (bottom) and the absorbance spectra of diamond nanocrystals (lower trace) measured at 300 K (from Guillois et al 1999).

at an equilibrium temperature of 1000 K. Atomic hydrogen recombination lines observed in this object indicate strong UV fluxes and a high temperature, which eventually anneal preexisting diamond grains (Guillois et al 1999). It has been recently demonstrated that carbon onions act as nanoscopic pressure cells and can be converted to diamonds during thermal annealing and irradiation with electrons (Banhart & Ajayan 1996).

Carbonaceous Solids   Carbonaceous dust in the interstellar medium may show strong diversity and may include amorphous carbon (AC), hydrogenated amorphous carbon (HAC), coal, soot, quenched-carbonaceous condensates (QCC), diamonds, and other compounds. The coexistence of PAHs and fullerenes together with complex carbonaceous dust suggests a common link and an evolutionary cycle that is dominated by energetic processing (Jenniskens et al 1993, Scott et al 1997). A detailed comparison of solid-state carbonaceous models of cosmic dust has been summarized by Papoular et al (1996). Solid carbon material such as graphite, diamonds, fullerite solids, and carbynes is discussed by Henning & Salama (1998). Figure 8 displays the chemical structure of some carbon compounds that are likely present in space.

Enormous progress has been made in the characterization of carbonaceous solids through laboratory studies (Henning & Schnaiter 1999), and new data show a strong link between the many different carbon phases (e.g. Ugarte 1992, 1995; Wdowiak et al 1995, Banhart & Ajayan 1996, Scott et al 1997). The improvement

PAHs   FULLERENES   SHORT CHAINS

DIAMONDS   GRAPHITE   SOOT

BUCKY TUBES   COMPLEX BUCKY TUBES   ONION TYPE C PARTICLES

Figure 8   Some of the various forms of carbon that are likely present in gaseous and solid state in the ISM and in solar system material.

in instruments and new techniques, used to investigate material relevant to the astronomical solid state, reveal a rich diversity of carbonaceous material on the nanoscale (Herlin et al 1998, Jaeger et al 1998, Wada et al 1999). Carbon structures in soot material were recently investigated by electron microscopy, and displayed different well-defined structures (Rotundi et al 1998). Future progress in this field will strongly influence the characterization of carbonaceous matter in space, and will help to resolve the carbon crisis and the remaining spectroscopic mysteries such as the UV bump, the ERE, the DIBs, and the UIR bands.

3.   ORGANIC MOLECULES IN COMETS

The modern view of the composition of comets began with the "dirty Snowball" model of Whipple (1950a,b). This model proposed that cometary nuclei were predominantly made of water ice with an admixture of small rock particles. An evaluation of the most important issues in cometary astronomy during the last 4 decades is reviewed by Festou et al (1993a,b). Today this model has been refined, and the nuclei of comets are thought to be composed of ice, rock, and large organic entities (commonly referred to as CHON particles), since these nuclei are composed primarily of carbon, hydrogen, oxygen, and nitrogen (Mumma 1997, Irvine et al 2000). The chemical composition of a comet nucleus has been recently constrained by Greenberg (1998), who proposes that 26% of the mass is incorporated in silicates, 23% in refractory material, 9% in small carbonaceous molecules, and $\sim$30% in H_2O ice (with small contributions of CO, CO_2, CH_3OH, and other simple molecules). Remote observations of cometary gas and dust from ground-based and space telescopes throughout the electromagnetic spectrum are used to constrain the formation and composition of comets. Recent results have shown that the volatile component in comets is dominated by water, followed by CO and CO_2, with trace amounts of other chemical species such as CH_3OH, CH_4, C_2H_2, etc (see Table 2). The trace molecules are important, however, because they give clues as to the conditions under which comets were formed. CO is the most abundant carbon species in the coma, but it has an extended source; only less than 7% CO relative to water ice is assumed to originate from the nucleus (Irvine et al 2000). In Hale-Bopp 50% of the CO originated from the nucleus (DiSanti et al 1999).

The origin of comets and the extent to which they have been altered during the formation process is far from being understood. Three models have been considered for the origin of comets: (1) the interstellar model, which suggests that interstellar grains agglomerated to form cometary nuclei in the cold outer solar nebula far from the protosun (Greenberg 1982); (2) the complete chemical equilibrium model, in which presolar material is altered and chemically equilibrated (Lunine et al 1991); and (3) an intermediate model in which presolar material has been chemically and physically processed (Chick & Cassen 1997, Fegley 1999). It is currently assumed that comets are a mixture of interstellar and nebular material (Mumma et al 1993,

Irvine 1999, Ehrenfreund & Schutte 2000b). The original composition of comets may differ according to their place of origin.

Comets appear to originate from two distinct sources: the Oort cloud, the source of long-period comets (periods P > 20 years); and the Kuiper Belt, the source of short-period comets (P < 20 years) (Cochran et al 1995, Weissmann 1995). A better discriminant between cometary sources is the Tisserand invariant; short-period comets generally have a value greater than 2 (e.g. Weissmann 1999). Evidence for two classes of comets is found from their whole coma scattering properties at large phase angles (Levasseur-Regourd et al 1996). Comets with higher maximum of polarization seem to be dust-rich (Bockelée-Morvan et al 1995). The properties of 85 comets showed a dust/gas ratio that does not vary with the dynamical age of the comet (A'Hearn et al 1995) and indicates that the composition of comets may be related to their place of formation. For example, the presence of carbon-chain molecules (C_2, C_3) shows a dramatic decline as the Tisserand invariant increases above 2 (A'Hearn et al 1995). New dynamical studies suggest that the source of the Oort cloud comets was the entire giant planet region from Jupiter to Neptune. It seems that comets are formed in different nebular environments and probably experienced thermal and collisional processing before their ejection to the Oort cloud (Weissmann 1999). Processing and dynamical exchange of icy planetesimals in the giant planet zone may have "homogenized" cometary nuclei. Future observations of short-period comets, which have a different evolution (Levison & Duncan 1997), and dynamically new long-period comets will allow us to address the question of the diversity of comets.

The only way to measure the nuclear composition directly is via in situ measurements by a space probe, such as the GIOTTO mission to comet Halley (Keller et al 1987). However, by observing the coma one can in principle deduce the molecular inventory of the nucleus. Remote sensing by gas phase molecular spectroscopy is less ambiguous than mass spectrometry. IR observations can directly sample molecules coming off the nucleus (Mumma et al 1996, Mumma 1997, Crovisier 1998). The predominant chemical processes occurring in the coma are photodissociation and photoionization of parent molecules as they are exposed to the solar radiation field. The first simple analytical model of coma chemistry was given by Haser (1957), who considered only photodissociation of parent molecules to form "daughter" and "granddaughter" molecules. It is now appreciated that in the high-density inner coma ($\sim 10^{13}$ particles cm^{-3}), ion-molecule and neutral-neutral reactions are also likely to be important (e.g. Schmidt et al 1988).

In this section we summarize current knowledge concerning the organic inventory of the comae of recent comets, both refractory species and volatile molecules, and compare it with that found in the interstellar medium.

3.1 Cometary Dust and Refractory Organics

The cometary nucleus is a porous aggregate of ices and refractory material. In situ measurements on past space missions and observations strongly enhanced

our knowledge about the structure and composition of comets. Several spacecraft performed a close flyby of Comet Halley in 1986. The particle composition was studied with mass spectrometers PUMA-1, PUMA-2, and PIA, flown on VEGA-1, VEGA-2, and GIOTTO, respectively. Time-of-flight mass spectra were recorded during the impact of dust particles on metal targets. All three instruments obtained a large collection of mass spectra of individual cometary dust particles in the mass range $3 \times 10^{-16} - 3 \times 10^{-10}$ g. These data revealed an overall mass ratio between 2 and 1 of siliceous to organic materials in Comet Halley dust (Fomenkova & Chang 1993).

In situ measurements made at Halley showed that about 70% of the dust grains comprised a mixed phase of organic material and refractory silicates; the remaining grains contained no organics (e.g. Jessberger et al 1988, Mumma et al 1993). An important discovery made by these encounters was the detection of CHON particles—that is, dust composed of carbon, hydrogen, oxygen, and nitrogen (Clark et al 1987, Langevin et al 1987, Jessberger et al 1988). Reanalysis of space-recorded data shows that CHON particles and silicate components are interdispersed at the submicrometer scale (Lawler & Brownlee 1992). Silicates, which comprise a major fraction of the refractory part of comets, appear to be a mix of high-temperature crystalline enstatite, forsterite, pyroxene, and glassy amorphous carbon (Hanner et al 1994, Crovisier et al 1997, Wooden et al 1999, Hanner 1999). Recent ISO observations showed crystalline silicates in comet Hale-Bopp as well as around young and evolved stars (Waelkens et al 1996, Waters et al 1996). The strong spectroscopic similarity of silicate material in all these objects has been reported (Malfait et al 1998). As the physical properties of disks around young stars and red giants are similar, Molster et al (1999) suggest that low temperature crystallization of silicate grains may occur in protoplanetary systems.

The data gathered by the PUMA mass spectrometer on the more refractory organic material existing in the coma of P/Halley constitute a unique data set (Kissel & Krueger 1987). Until future space missions are completed (e.g. STARDUST and ROSETTA), any review is limited to the Halley results (Kissel et al 1997, Cottin et al 1999). The PUMA data allowed the tentative, but not unambiguous, identification of many distinct organic molecules emanating from the carbonaceous dust (Kissel & Krueger 1987). The organic inventory has been summarized by Kissel & Krueger (1987), Cottin et al (1999), and Fomenkova (1999). The majority of grains contain heteropolymers and different mixtures of carbon phases and compounds including alcohols, aldehydes, ketones, and acids. Other organic species identified include PAHs, highly branched aliphatic hydrocarbons, and unsaturated hydrocarbon chains, including alkynes, dienes, various large nitriles, and analogous species with imino and amino end-groups. Several nitrogen heterocycles may also have been identified; these include pyrrole, pyrroline, pyridine, pyrimidine, imidazole, and perhaps purine and adenine.

Erosion or fragmentation of the mixed-phase particles may give rise to complex molecules in the coma (Festou 1999). This mechanism has been invoked to explain the existence of extended coma sources for various molecules: CO, H_2CO,

CN, C_2, C_3, and NH_2 (Mumma et al 1993). Extended sources may not reflect nuclear ice abundances (DiSanti et al 1999). This provides more indirect evidence that extremely complex organic molecules could be released from cometary dust particles. These include polyoxymethylene (POM), a polymer of H_2CO, whose decomposition was originally proposed by Huebner et al (1987) as an explanation of the extended formaldehyde source around comet Halley. Other complex molecules are probably being fragmented as well (Huebner et al 1989) and may include HCN-polymers (Matthews & Ludicky 1992). Eberhardt (1999) argues that photodissociation of H_2CO into CO can account for most of the extended CO source observed in comet Halley. Recently, Bernstein et al (1995) suggested hexamethylenetetramine (HMT, $C_6H_{12}N_4$) as a candidate component of cometary organics. In laboratory experiments on interstellar/cometary ice analogues, HMT is formed by strong UV photolysis and warming of ammonia/methanol-rich ices. Various POM-related compounds are also formed, but not at the concentrations seen in ammonia/formaldehyde-rich ices where thermally promoted reactions are predominant (e.g. Allamandola et al 1997). These latter reactions are also candidates for the origin of the POM identified in Halley; it is therefore likely that the CHON particles contain a mixture of polymers (Eberhardt 1999). The claimed identification of a polycylic aromatic hydrocarbon in Halley's comet (Moreels et al 1994) raises the possibility that other polyaromatic organics are also present in cometary dust. The 3.4 μm emission feature in comets, which shows a profile like the interstellar diffuse cloud absorption (see Section 2.2.1), was originally attributed to hydrocarbons in dust grains (Knacke et al 1986). Reanalysis of this feature showed that most of this emission can be attributed to CH_3OH (Reuter 1992, Bockelée-Morvan et al 1995) and other molecular organic species (DiSanti et al 1995, Mumma et al 1996). The exact composition of cometary refractories will be investigated by current and future space missions such as STARDUST and ROSETTA (Huntress 1999).

3.2 Cometary Volatiles

3.2.1 Interstellar Organics?

The recent apparitions of comets Hyakutake and Hale-Bopp have revolutionized our understanding of the volatile chemical inventory of comets and the interstellar-comet connection. Observational and theoretical work on the nucleus and coma of Hale-Bopp is extensively summarized in the proceedings of the International Conference on Comet Hale-Bopp published in volumes 77–79 of *Earth, Moon and Planets* (1999). Here we discuss selected results in the wider context of organic astrochemistry.

As a comet approaches the sun, solar radiation heats the surface layers of the nucleus and induces sublimation of the molecular ices. The gaseous molecules then stream away from the nucleus and carry the entrained dust grains with them. Remote sensing of the bright target Hale-Bopp showed that at large heliocentric distance the activity is driven by sublimation of CO. As the comet approaches the

sun, the CO outgassing rate increases roughly as r_h^{-2}. Closer to the sun, crystallization of amorphous water ice is predicted to occur, and the release of trapped CO can then become the major CO source. At about 2.5 AU from the sun, sublimation of water ice from the surface layer becomes more and more efficient, and water outgassing becomes the major driver of the comet's activity (Biver et al 1997, Enzian et al 1998, Huebner & Benkhoff 1999). Figure 9 shows the evolution of the theoretical CO and water outgassing rates (Enzian 1999) compared to the observed rates (Biver et al 1999).

The model confirms that sublimation of CO ice at large heliocentric distance produces a gradual increase in the comet's activity as it approaches the Sun. Crystallization of amorphous water ice is predicted to begin at 7 AU from the Sun,
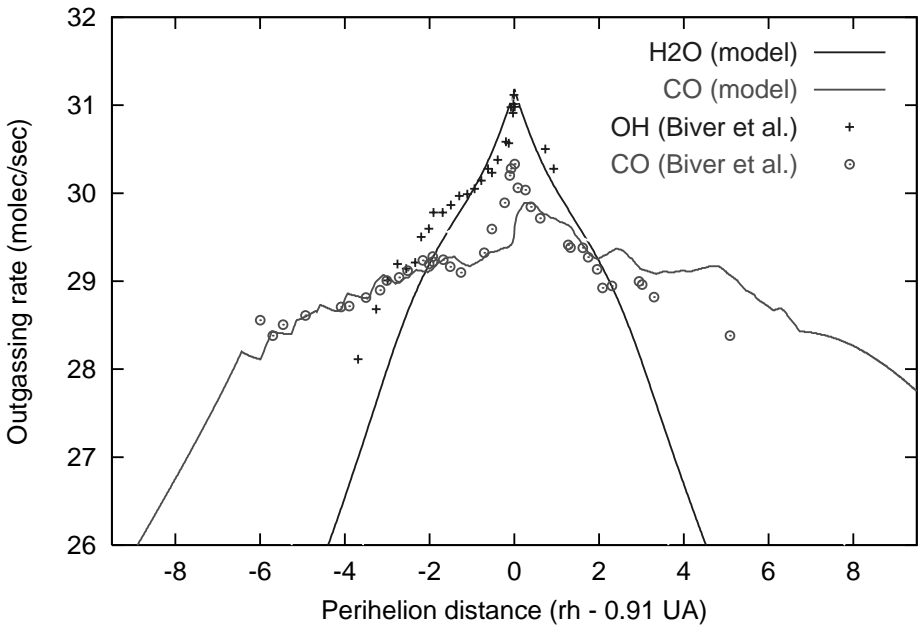
Figure 9 Evolution of the modeled CO and water outgassing rates (Enzian 1999) of comet Hale-Bopp compared with measured outgassing rates from astronomical observations (Biver et al 1999). The modeled comet nucleus has an albedo of 0.04 and a radius of 35 km; the radius is suggested by CCD observations (Weaver & Lamy 1999). The initial nucleus composition contains dust (50% by mass), amorphous water ice (40%), CO trapped in amorphous water ice (5%), and an additional small amount of CO ice (5%) in an independent phase. The thermal evolution is computed for two apparitions from 50 AU pre-perihelion to 50 AU post-perihelion. During the first orbit (which is shown above) the spin axis of the model comet nucleus is perpendicular to the orbital plane, whereas in the second orbit (which is shown above) the spin axis lies in the orbital plane and points toward the Sun at perihelion (from Enzian 1999).

but no outbursts were found. Seasonal effects and thermal inertia of the nucleus material lead to larger CO outgassing rates as the comet recedes from the Sun. Radio observations of comet Hale-Bopp by Biver et al (1997) showed that between 1.4 and 4 AU, the production rates of many simple molecules exhibited different dependencies on the heliocentric distance.

Many new cometary molecules were discovered or better constrained by IR and radio observations of comets Hyakutake and Hale-Bopp (Mumma et al 1996, Irvine et al 1996, Brooke et al 1996, Crovisier et al 1997, Bird et al 1997, Biver et al 1997, 1999, Lis et al 1997, Mumma 1997, Dello Russo et al 1998, Bockelée-Morvan et al 1998, DiSanti et al 1999, Magee-Sauer et al 1999, Dello Russo et al 2000, Crovisier & Bockelée-Morvan 1999, Bockelée-Morvan et al 2000). To understand the differences between cometary and interstellar material, we must first make a detailed abundance comparison between cometary volatiles and the molecular ices found in various regions of the dense ISM (Despois 1992, Mumma et al 1993, Mumma 1997, Crovisier 1998, Ehrenfreund et al 1997c, Ehrenfreund & Schutte 2000b, Irvine 1999, Irvine et al 2000). Table 2 shows such a comparison, including the gas phase abundances of selected molecules found in hot molecular cores where icy grain mantles have been evaporated. Generally, there are fewer unambiguous detections of large organics in cometary comae than in hot cores. This is due to difficulties in making radio observations of molecules in the more diffuse coma and the fact that abundances of large molecules probably decrease with increasing complexity. Despite this, significant upper limits have been obtained in Hale-Bopp for many organics (Crovisier 1998, Crovisier & Bockelée-Morvan 1999). Cometary spectra also contain many unidentified lines (e.g. Wyckoff et al 1999), so more organics may await discovery at shorter wavelengths.

It appears that interstellar and cometary species have similar compositions. The presence of HCOOH, HNCO, and NH_2CHO, as well as formaldehyde and methanol, is consistent with an origin on interstellar grains where hydrogen atom additions to CO, followed by C, O, and N atom additions, dominated the chemistry (see Section 2.1.1). The discovery of C_2H_6 (Mumma et al 1996) also lends support to the idea that the nuclear ices were formed in cold molecular clouds, since it could result from the reduction of acetylene on grains. Other molecules, if formed under interstellar conditions, appear to require gas phase synthesis prior to incorporation into ices; these include C_2H_2, CH_3CN, HC_3N, $HCOOCH_3$, and HCN (see Section 2.1.3)—although there is some debate as to whether $HCOOCH_3$ forms by gas phase reactions (MacDonald et al 1996, Helmich & van Dishoeck 1997).

Some notable exceptions in the abundance of interstellar ices and cometary volatiles are the large amounts of methanol and ammonia recently observed from the ground toward certain protostars (Dartois et al 1999a, Lacy et al 1998). Interstellar abundances of CH_3OH, which are consistent with cometary data, are currently observed predominantly in low-mass protostars. More thorough observations of such objects with the new class of 8+ m telescopes (VLT, KECK, SUBARU etc.) are needed in the future to investigate these discrepancies. OCS seems generally more abundant in comets than in interstellar ices toward YSOs,

whereas the reverse holds true for CO_2, HCOOH, and HNCO (Ehrenfreund & Schutte 2000b). There are also significant differences between the cometary abundances of trace molecules when compared with abundances of hot core gas: some are markedly higher (HCOOH, NH_2CHO, HNCO), whereas others are much lower (CH_3CN, C_2H_2, HCN). This indicates that some cometary ice molecules are the result of a significant amount of processing. It is unclear whether these abundance differences reflect a different chemistry in the Sun's parent interstellar cloud or modifications induced as this material became incorporated into the protosolar disk. A further possibility is that some of these molecules (e.g. CH_3CN, HC_3N, $HCOOCH_3$) could be produced in the coma by gas phase reactions (see Section 3.2.2). Fully quantifying ISM-comet abundance differences will probably require detailed chemical modeling of the infall of interstellar gas and dust through the accretion shock into a protostellar disk, and of the chemical evolution followed in the comet-forming regions (e.g. Aikawa & Herbst 1999a). Such work may also shed light on the compositional differences in trace species to be expected as future comets are subjected to detailed chemical scrutiny.

3.2.2 The Origin of HNC

Simple organic molecules may also provide important probes of cometary composition and origin. Cold interstellar clouds have large HNC/HCN ratios ~ 0.1–1 (Ohishi & Kaifu 1998). The detection of HNC in comets and the associated HNC/HCN ratios (0.06–0.2) (Irvine et al 1996, Biver et al 1997, Hirota et al 1999, Irvine et al 1999) therefore strongly suggested an ion-molecule origin for the HNC in a cold molecular cloud. However, in the dense inner coma, chemical reactions could occur that synthesize HNC from HCN; the HNC/HCN ratio in comets has been viewed from this perspective (Rodgers & Charnley 1998, Irvine et al 1998a,b). Ion-molecule reactions can produce some HNC from HCN but cannot produce the observed HNC/HCN ratio in Hyakutake. The prodigious molecule production rate in comet Hale-Bopp suggests that isomerization of HCN by suprathermal hydrogen atoms could reproduce both the observed HNC/HCN ratio and its variation with heliocentric distance (Rodgers & Charnley 1998); however, this mechanism fails to produce the HNC/HCN ratio in Hyakutake's coma (0.06), which suggests another source for the HNC in this comet. Comet Lee has a water production rate similar to that of Hyakutake but an HNC/HCN ratio of about 0.12 (Crovisier 2000). Hence, the above gas phase reactions would also fail to reproduce the comet's HNC/HCN ratio. These studies suggest that there may be two sources of cometary HNC: nuclear sources and coma-synthesized sources. Indeed, interferometric observations of Hale-Bopp by Blake et al (1999) indicate two HNC components: one corresponding to nuclear emission and another corresponding to more extended or jet emission. It is interesting that the HNC/HCN ratio of the nuclear component is similar to those of comets Hyakutake and Lee, whereas the jet component is almost two to three times as large. Hence, in comets with large water production rates, the nuclear HNC component may be overwhelmed

by that due to coma synthesis. Alternatively, Blake et al (1999) favor an explanation based on trapping of a large (interstellar) nuclear HNC/HCN ratio, which is then modified during sublimation. More measurements of this important ratio are clearly needed from more comets.

3.2.3 Isotopic Ratios

Enhanced isotopic fractionation ratios provide strong evidence that cometary material can retain a chemical memory of an origin at the cold temperatures of interstellar clouds (Crovisier 1998). Comets Halley, Hale-Bopp, and Hyakutake had water D/H ratios of $\sim 3 \times 10^{-4}$ (Bockelée-Morvan et al 1998, Irvine et al 2000), similar to those of hot cores (Gensheimer et al 1996). Blake et al (1999) have proposed that the nuclear ice HDO/H_2O ratio in Hale-Bopp is ~ 1.5–2.5×10^{-3}, and there is recent evidence that interstellar ices could have significantly higher HDO/H_2O ratios (Teixeira et al 1999); however, it is difficult to reconcile these with the lower values seen in hot core gas. Meier et al (1998) measured DCN/HCN $\sim 2 \times 10^{-3}$, which is lower than that found in interstellar clouds ($\sim 2 \times 10^{-2}$). Hence, although these D/H ratios support an interstellar origin, it appears that the material either was processed sufficiently to lower these values prior to comet assembly, or was simply formed in higher-temperature interstellar gas (Millar et al 1989). Recently, Aikawa & Herbst (1999b) showed that cometary D/H ratios can be produced in the outer regions of protostellar disks, which supports the view that cometary volatiles are a mixture of interstellar matter and matter that is processed in situ. Finally, other isotopic ratios in oxygen, nitrogen, sulfur, and carbon have been measured in simple cometary organics and found to be consistent with cosmic (solar) values (see Crovisier & Bockelée-Morvan 1999).

By characterizing the organic composition, isotopic fractionation, and spin ratios of future comets, it may eventually become possible to identify the formation sites of individual comets and to quantify the degree to which their nuclei differ from pristine interstellar material.

4.   ORGANIC MOLECULES IN METEORITES

It was established over a century ago that some meteorites contain carbonaceous material. Organic compounds that have been identified in carbonaceous C1 and C2 chondrites include amines and amides; alcohols, aldehydes, and ketones (Cronin & Chang 1993); aliphatic and aromatic hydrocarbons (Hahn et al 1988, Kerridge et al 1987, Gilmour & Pillinger 1994, Messenger et al 1998, O'D Alexander et al 1998, Sephton et al 1998, Stephan et al 1998); sulfonic and phosphonic acids (Cooper et al 1992); amino, hydroxycarboxylic, and carboxylic acids (Cronin & Pizzarello 1990, Cronin et al 1993, Peltzer et al 1984); purines and pyrimidines (Stoks & Schwartz 1979, 1981); and kerogen-type material (Becker et al 1999b).

The study of presolar grains in meteorites allows us to trace the circumstellar origin of some dust species (Bernatowicz & Zinner 1996, Bernatowicz 1997). The

isotopic composition of presolar graphite grains, diamonds, and SiC grains isolated from meteoritic samples indicates their interstellar origin and a mass ratio of graphite:SiC:diamonds = 1:5:400 (Ott 1993). Nanodiamonds are present in primitive meteorites in abundances of up to ∼1400 ppm (Huss & Lewis 1995). These grains contain an anomalous Xe isotopic component (Xe-HL) considered to be characteristic of nucleosynthetic processes in supernovae (Lewis et al 1987). The ^{15}N depletion and the low C/N ratio in such grains is consistent with carbon-rich stellar environments. Only low abundances are observed for graphite in meteorites (Nuth 1985); however, the greatest concentrations of noble gases are measured in the poorly graphitized carbon (PGC) that makes up the bulk of the carbon material in these meteorites. SiC is present in many carbon stars and some PN, but has not been observed in the ISM. Conversely, presolar micron-size SiC grains are found in abundance in carbonaceous chondrites. Elemental and isotopic ratios of noble gases in most meteoritic SiC grains show excellent agreement with predictions for material enriched with s-process nucleosynthesis dredged up from the helium shells of AGB stars during thermal pulses (Ott 1993). GEMS (Glasses with Embedded Metal and Sulfide) are a subgroup of polyphase grains occurring in interplanetary dust particles, whose depletion and inclusions indicate their interstellar origin (Bradley 1994, Bradley et al 1999).

Through the use of laser desorption mass spectrometry (LDMS), PAHs, kerogen-like material, fullerenes, and fulleranes have been detected in meteorites (Becker 1999). The presence of carbon onions in acid residues of the Allende meteorite suggested that higher fullerenes or nanotubes may be present in meteorites. This has been recently confirmed by LDMS measurements of the higher fullerenes (C_{100} to C_{400}) in the Allende meteorite (see Figure 10; Becker et al 1999a). In addition, the higher fullerenes have also been isolated from the Murchison carbonaceous residue, and measurements of noble gases (helium, neon, and argon) in both the Murchison and Allende fullerenes indicate that these molecules are indeed extraterrestrial in origin (Becker et al 2000). The meteoritic PGC material retains the newly detected fullerene component; fullerenes may therefore represent an important carrier phase for noble gases that has been previously overlooked (Becker et al 2000).

Many classes of organic molecules have been discovered in the Murchison carbonaceous chondrite (Cronin & Chang 1993). One explanation for the origin of these compounds is that they were formed from organic matter residing on interstellar dust grains that survived entry into the region of the protosolar nebula where comets and other icy bodies formed and that ultimately became incorporated into the parent bodies of carbonaceous meteorites (Bunch & Chang 1980). The Murchison organic inventory displays a large deuterium enrichment, particularly in the amino and hydroxycarboxylic acids. This constitutes one of the most convincing pieces of evidence that the original carbon reservoir was interstellar (Kerridge & Chang 1985, Zinner 1988) because in cold clouds, enhanced molecular D/H ratios can easily be attained by gas phase and grain-surface processes (Millar et al 1989, Tielens 1983). In the "interstellar-parent body" scenario, melting of the parent
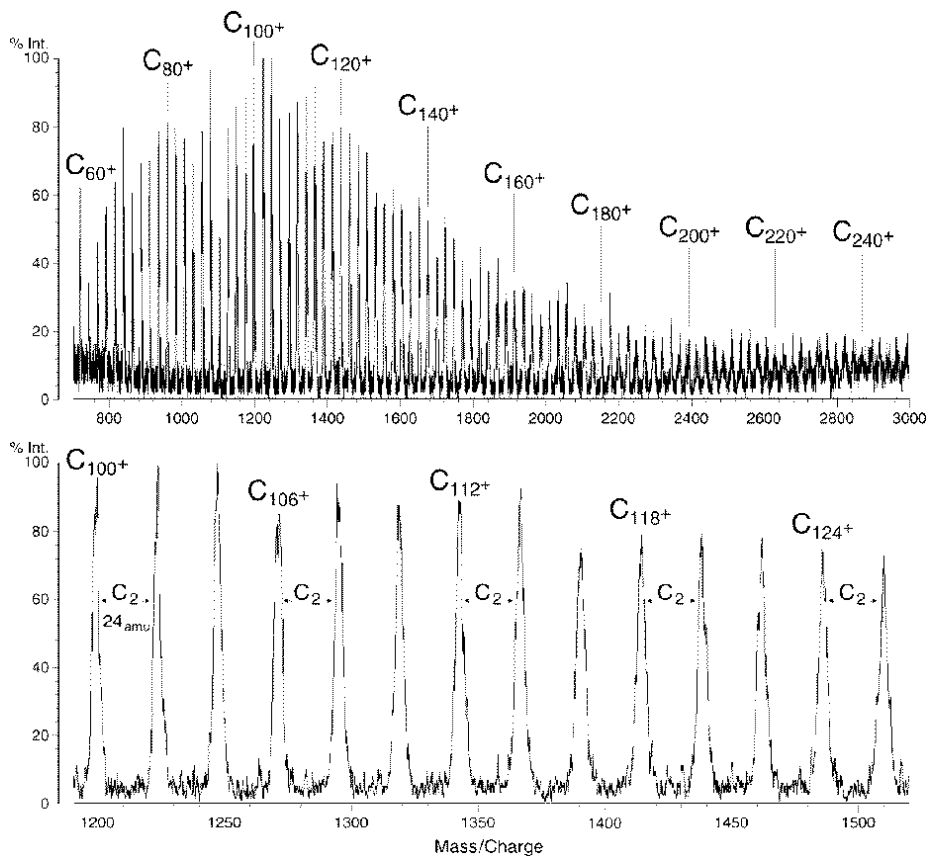
Figure 10   The detection of higher fullerenes in the Allende meteorite was recently reported by Becker et al (1999a). The figure shows laser desorption time-of-flight mass spectra of the meteoritic extract. A small peak for C_{60}^+ and remarkably stable larger carbon clusters between C_{100}^+ and C_{250}^+ (*top*) are displayed, as well as a closer examination of the larger clusters (*bottom*).

body water ice resulted in the relatively pristine interstellar material undergoing a variety of organic reactions in solution ("aqueous alteration"), leading to the formation of a second generation of more complex organics. Therefore, many of the organics identified in Murchison have been postulated to be either truly inter-stellar components (e.g. alcohols, aldehydes, and amines) or altered parent body products, such as urea and guanylurea and amino acids, which were derived from various interstellar precursors (NH_3, HNCO, NH_2CN, acetone, acrolein, vinyl cyanide).

Detailed analyses of Murchison extracts have shown very marked trends within each class of organic compound, as well as some characteristics that are quite general (Cronin & Chang 1993, Cronin et al 1995). For a given number of carbon

atoms there is complete structural diversity within most classes of organic com-
pounds, which indicates formation mechanisms involving free C-bearing radicals.
All stable isomeric forms are present, and branched-chain isomers are the most
abundant. Within each homologous series, the molecular concentrations decline
with the increasing number of carbon atoms, which is consistent with chain growth
by single-carbon additions. These characteristics are particularly evident in the
large number of amino acids identified in the extracts obtained from carbonaceous
chondrites, such as Murchison. An extraterrestrial (though not necessarily inter-
stellar) origin is suggested for many of these amino acids because, for example,
α-aminoisobutyric acid (AIB) and isovaline are present in appreciable abundances
(e.g. Cronin & Pizzarello 1983) but are particularly rare on Earth (Brinton et al
1998); other amino acids are unknown in terrestrial biochemistry.

Strecker-cyanohydrin synthesis of meteoritic α-amino and α-hydroxy acids dur-
ing aqueous alteration of a parent body is an appealing scenario (Cronin & Chang
1993). It accounts for the strong structural correspondence between amino and hy-
droxy acids at a given carbon number, and the fact that both exhibit high isotopic
fractionation. This latter facet strongly supports the hypothesis that interstellar
molecules were the simple precursors required for Strecker-cyanohydrin processes
(Cronin 1989). There are two problems with this scenario, however (Cronin &
Chang 1993, Kerridge 1999). First, the ^{13}C and D fractionation data appear to be
inconsistent with a common (aldehyde or ketone) precursor—the amino acids are
far more highly enriched in D and ^{13}C. This places doubt on there being a common
precursor for each type of acid (Cronin et al 1993). Second, imino acids should
also be produced in this synthesis but are not abundant in Murchison (Kerridge
1999). The connection between meteoritic amino acids and interstellar chemistry
would be strengthened with the discovery of interstellar glycine (see Snyder 1997).
If alkyl cation transfer reactions with glycine can proceed, driven by evaporated
alcohol-rich ice mantles, (see section 2.1.3), they could lead to other meteoritic
amino acids in hot cores; these include α-alanine, α-aminoisobutyric acid, and 2-
aminobutyric acid (Charnley 2000). These molecules may be detectable with future
millimeter-wave arrays. Recently it has been claimed that equilibrium (Strecker)
reactions could produce amino acids and hydroxy acids in interstellar molecular
gas (Chakrabarti & Chakrabarti 2000). The reactions and rates employed in that
particular study included those from a model of amino acid synthesis in submarine
hydrothermal systems of the Earth's early oceans (Schulte & Shock 1995). It is
inappropriate to extrapolate data from equilibrium chemistry in liquids to inter-
stellar plasmas, where the chemistry is always far from equilibrium, and so the
claim of Chakrabarti & Chakrabarti (2000), that interstellar glycine, alanine, and
also the DNA base adenine, could be formed by these reactions is most probably
incorrect.

Recent meteoritic organic studies have also specifically addressed the ques-
tion of their relation to the development of life. Enantiomeric excesses of 7–9%
have recently been measured in several Murchison amino acids known to be of ex-
traterrestrial origin (e.g. 2-amino-2,3-dimethylpentanoic acid; Cronin & Pizzarello

1997). This fact suggests an extraterrestrial provenance for the homochirality found in protein amino acids, or at least a primordial L/D excess that could subsequently be amplified by further reactions. The PAH component of meteorites (e.g. Krishnamurthy et al 1992, McKay et al 1996, Clemett et al 1998) has been invoked as an integral part of the claim that the Martian meteorite ALH84001 contains extinct microbial life—a claim that is currently the subject of intense debate (Jull et al 1998, Bada et al 1998, Becker et al 1999b).

In conclusion, carbonaceous meteoritic material represents a sample of interstellar matter—albeit a highly processed one. Future studies will undoubtedly expand the catalogue of molecules found in this material, along with its connection to comets and the interstellar medium.

5.   THE VOYAGE

The life cycle of interstellar dust is tied to the evolution of stars and planets in the Galaxy. Molecules with up to 15 carbon atoms have been observed in cold clouds and hot cores in the ISM. What degree of complexity can be reached by reactions in molecular cloud gas is not evident, but might be explored by future millimetric observations aimed to search for larger species. Hydrogenation and oxidation reactions lead to simple organic species on the grain surface (Tielens & Hagen 1982, Charnley 1997, Schutte 1999). Energetic processing and heating of complex ice mixtures in laboratory experiments revealed the presence of complex molecules such as alcohols, ketones, polyoxymethylene (POM), and HMT ($C_6H_{12}N_4$) (Bernstein et al 1995, 1997). Because energetic processing in dense clouds is not well constrained, those laboratory experiments may however, only partly reflect the conditions in dense clouds.

In diffuse clouds and circumstellar shells, a variety of carbon compounds are observed. Among the most abundant organic molecules are PAHs (Tielens et al 1999), which are also identified in meteorites (Krishnamurthy et al 1992), and interplanetary dust particles (IDPs) (Clemett et al 1993), possibly in comets (Moreels et al 1994) and in the atmosphere of Titan and Jupiter (Sagan et al 1993). Other important carbon species likely present in molecular clouds are fullerenes and diamonds (Foing & Ehrenfreund 1997, Guillois et al 1999). A large fraction of the cosmic carbon seems to be tied up in carbonaceous solids that may be present in many different structures (Henning & Salama 1998).

The study of cometary nuclei and their comae is of fundamental importance because comets are thought to be the most pristine members of the solar system (e.g. Delsemme 1982). Carbonaceous chondrites are unique with respect to their content of carbon in the form of organic compounds. A central question is: How much of the organic material present in primitive bodies, such as comets, asteroids, and meteorites, is pristine interstellar material, and to what extent is the chemical inventory of these objects a result of chemical processing within the nebula (Fegley & Prinn 1989, Mumma et al 1993, Irvine et al 2000)? While in some models comet

material is assumed to be basically unprocessed interstellar ice and dust (Greenberg 1982), other models state that the original interstellar ices were processed in the solar nebula before becoming incorporated into the cometary body (Engel et al 1990, Lunine et al 1991, Chick & Cassen 1997, Fegley 1999). To address this problem in a quantitative manner, we need a detailed understanding of the relevant chemical reactions and processing that interstellar gas and dust experiences as it evolves from the diffuse ISM into cold molecular clouds, and thereafter into star-forming cores. Additionally, we need to obtain evidence showing the extent to which organics have been preserved in solar system bodies (Sandford 1996, Mumma 1997, Irvine et al 2000).

Cometary volatiles and their relative proportions are more compatible with interstellar solid state abundances (Mumma 1997, Ehrenfreund et al 1997c). A comparison of interstellar and cometary ices using recent ISO data has revealed a general correspondence in the composition of cometary and interstellar ices, but discrepancies are also apparent (see Table 2; Ehrenfreund & Schutte 2000b). If interstellar icy grains are incorporated unaltered into comets, ice species should be observed in comets at varying heliocentric distances because of their different sublimation temperatures (Ehrenfreund 1999a). A comparison of volatiles in the cometary coma and interstellar abundances shows that certain aspects of cometary activity are consistent with interstellar ice chemistry and gas species in hot cores. However, there is strong evidence that cometary ices are a mixture of original interstellar material with material that has been moderately to heavily processed in the presolar nebula (Irvine 1999, Ehrenfreund & Schutte 2000b, Ehrenfreund 2000, Irvine et al 2000).

The early Earth may have obtained most of its volatile organic material from the arrival of meteorites and comets at its surface. Some of this matter was accu-mulated in the form of surviving organic compounds (Anders 1989, Chyba et al 1990, Maurette et al 1995, Pierazzo & Chyba 1999). Determining the most likely distribution of meteoritic and cometary organic molecules that could seed primitive planets is a key astrobiological objective because it sets the initial conditions for at least part of their phase of prebiotic chemical evolution (Wood & Chang 1985, Cronin & Chang 1993, Oro & Lazcano 1997). Precursor molecules for life, includ-ing HCN, H_2CO, amino acids, and purines, have been identified in astronomical observations of the interstellar gas, in comets, and in laboratory investigations of extraterrestrial material. Recent laboratory experiments lend support to the idea that PAHs may have been important intermediates in the cHl pathways that led from space to the origin of life on Earth (Bernstein et al 1999). In H_2O-PAH icy mixtures, biogenic compounds were formed by UV radiation and may have found their way to the early Earth (Bernstein et al 1999, Ehrenfreund 1999b). The recent detection of higher fullerenes in meteorites shows that those compounds may have played an important role on the early Earth, and perhaps other planets, by providing not only a source of carbon but also the volatiles that contributed to the development of planetary atmospheres (Becker et al 2000).

6.   FUTURE STUDIES OF ORGANICS IN THE UNIVERSE

Current and future space missions are crucial to enhance our knowledge of organic compounds in the Universe. Although the analysis of ISO data will provide us with important information on organic molecules in space for at least a decade, the next IR satellite SIRTF is already on the start ramp. Further IR missions planned for the next millenium are the airborne observatory SOFIA and the FIRST satellite. Future ground-based IR facilities and (sub)millimeter interferometers, such as VLT, KECK and ALMA, will lead to the detection of complex molecules with abundances almost a factor of a hundred below current detection limits.

Milestones are expected in the search for extrasolar planets and in the planetary exploration of our own solar system. STARDUST is on its journey to comet Wild-2, and will capture comet dust and volatiles by impact into an ultra-low-density aerogel at a low speed of 6.1 km s^{-1} and an encounter distance of 150 km from the nucleus. The collected material will be dropped off in a reentry capsule that will parachute to Earth in 2006, and will allow the first analysis of cometary samples in Earth laboratories (http://stardust.jpl.nasa.gov/top.html). CASSINI-HUYGENS is on its way to meet Saturn and Titan in 2004. The HUYGENS probe will be released to parachute through the atmosphere of Titan with an entry speed of 20,000 km/h. Aerobraking will allow a 2.5-hour descent of the probe; meanwhile, six instruments will measure the chemical properties of Titan's atmosphere, which is known to contain organic molecules that reflect prebiotic conditions (http://sci.esa.int). The ROSETTA comet rendezvous mission will be launched in 2003 with the Ariane 5 rocket for a rendezvous maneuver with comet Wirtanen in 2011–2013. More than 20 instruments on the orbiter and the lander will obtain data on cometary origin and the interstellar-comet connection, which will broaden our insight into the origin of our solar system (http://sci.esa.int). Future Mercury missions (MESSENGER, BEPICOLOMBO) and lunar missions (SMART1, SE-LENE) will also investigate the presence of ice deposits (and eventually organics) in the permanently shadowed polar areas. Other important missions include the search for organics and extinct/extant life on Mars (MARS-EXPRESS/BEAGLE-2, Mars Sample Return 2005) and missions to Jupiter's moon Europa (EUROPA ORBITER) and the farthest planet in our solar system, Pluto (PLUTO-KUIPER EXPRESS).

In the life cycle of cosmic dust, organic molecules formed in the ISM are later incorporated in solar system material, and probably supplied organic material that seeded the early Earth (see Figure 11, color insert). The interdisciplinary effort combining astronomical observations, laboratory studies, and theoretical models in the 1990's has shown significant progress in our understanding of the ISM-planetary connection (Owen & Bar-Nun 1998, Cruikshank 1997, 1999, Ehrenfreund et al 1999b, McCord et al 1997, Irvine et al 2000, Lunine et al 2000) and will certainly continue to do so in the new millennium. The study of the formation, stability, and evolution of large carbon molecules in the universe therefore supports

our understanding of the physical and chemical processes in the ISM and in solar systems including ours, and so may shed some light on the emergence of life and our own existence.

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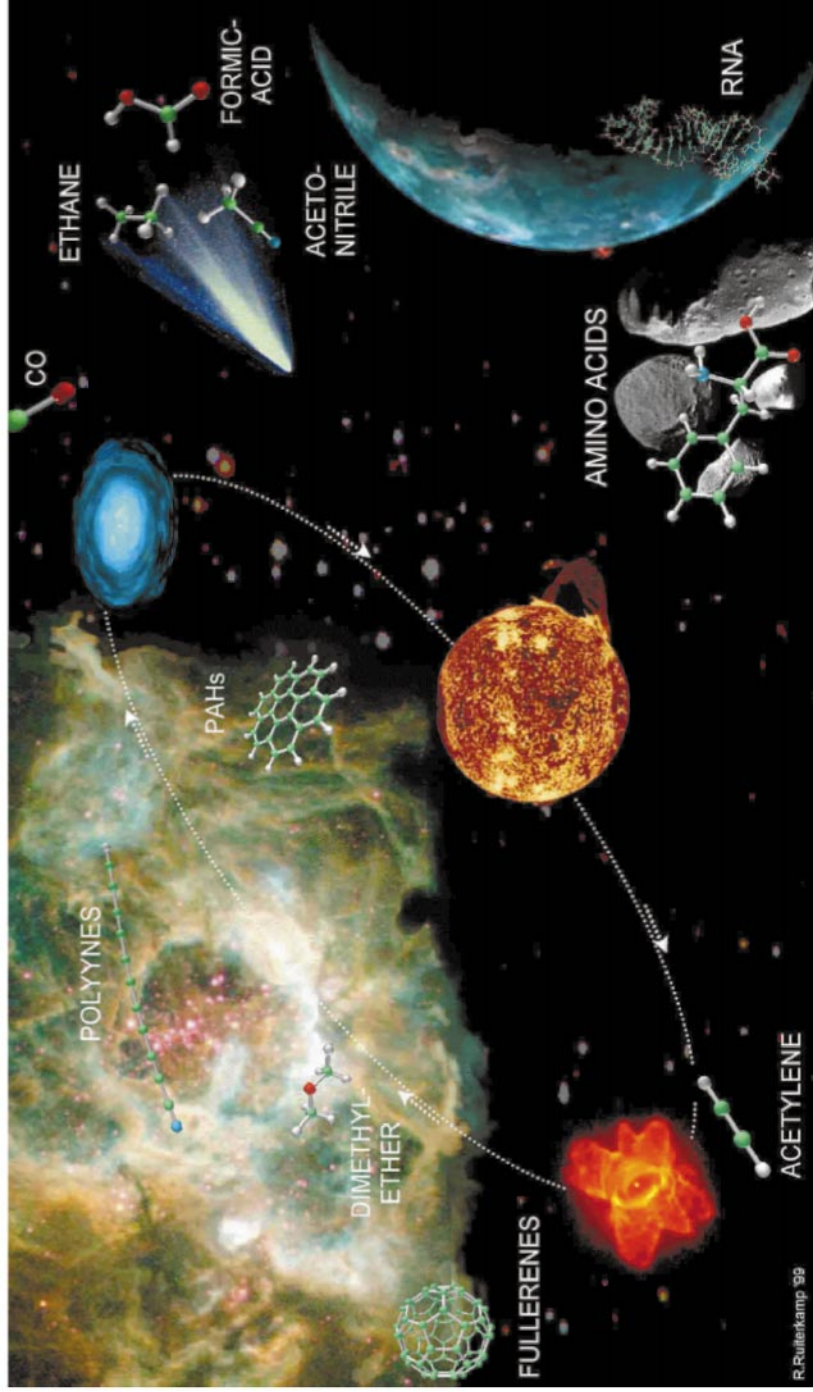
Figure 11 The cycle of organic molecules in the Universe. Interstellar organics are formed in the interstellar gas, in stellar outflows and on dust grains. This organic material is integrated in the Solar System and is partly chemically processed and/or destroyed. In the final stage of stars, dust and elements are returned to the interstellar medium. Organic molecules formed during this dust cycle may have seeded the early Earth.

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