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Interstellar Molecules [and Discussion]

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Interstellar molecules

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Some 70 different molecular species have so far been detected variously in diffuse interstellar clouds, dense interstellar clouds and circumstellar shells. Only simple (diatomic and triatomic) species exist in diffuse clouds because of the penetration of destructive ultraviolet radiations, whereas more complex (polyatomic) molecules survive in dense clouds as a result of the shielding against this ultraviolet radiation provided by dust grains. A current list of interstellar molecules is given together with a few other molecular species that have so far been detected only in circumstellar shells. Also listed are those interstellar species that contain rare isotopes of several elements. The gas phase ion chemistry is outlined via which the observed molecules are synthesized, and the process by which enrichment of the rare isotopes occurs in some interstellar molecules is described. Reference is also made briefly to some very recent work in interstellar ion chemistry. A list of the atomic and molecular species that have been detected in cometary atmospheres is given and attention is drawn to the similarities and differences between interstellar and cometary molecules. The physical and chemical processes by which these observed cometary species may be generated from material that sublimes from the cometary nucleus are discussed.

1. Introduction

Diatomic molecules were first observed in diffuse molecular clouds via their characteristic optical absorption spectra some 50 years ago (Swings & Rosenfeld 1937; Dunham & Adams 1937*a*, *b*). During the intervening period, and especially during the past 20 years, following the development of radio astronomical techniques, many complex (polyatomic) molecules have been detected (largely via their characteristic rotational emission spectra) in the cool denser regions of gas and dust in the Milky Way and also in other galaxies (see, for example, Rydbeck & Hjalmarson 1985). Until now about 70 different molecular species have been identified in the interstellar medium; particularly rich sources of molecules are the dense molecular clouds in the Orion, Sagittarius and Taurus regions. Molecular species are also very abundant in some circumstellar shells, notably that of the evolved star IRC+10216. The existence of molecules in all of these regions is of great significance to astrophysics because they are the means of probing the physical state of such regions. Hence a great deal of attention has been devoted to understanding how the molecules are synthesized at the very low temperatures of these regions which are not conducive to normal (neutral–neutral) chemistry. Much progress has been made as a result of close cooperation between research workers in several disciplines including radio-and millimetre-wave astronomers, spectroscopists, laboratory kineticists and theoreticians. It is now accepted that gas-phase ionic reactions are largely responsible for the production of most of the molecules so far detected in interstellar clouds, a conclusion reached on the basis of the agreement between observed abundances and those predicted by gas-phase ion-chemical models of individual molecular clouds (Millar & Freeman 1984). An interesting point to note immediately is that the individual molecular clouds do not have the same molecular compositions (Rydbeck & Hjalmarson 1985) and there are interesting implications of this heterogeneity. This is mentioned again in later sections.

Many molecular species have also been detected in cometary atmospheres (Huebner 1985) and some are common to both comets and interstellar clouds (Irvine *et al.* 1986). Other cometary molecules, not observed in interstellar clouds, could be fragments of well-known interstellar molecules (e.g. the cometary NH and NH_2 radicals could well be photofragments of parent NH_3 molecules, see §5). These similarities naturally raise the question as to whether comets are interstellar in origin. Comets could possibly have originated in cold interstellar gas and dust clouds where a wide variety of interstellar molecules existed, or in warmer gas (e.g. in the presolar nebula (Irvine 1983)), which previously had been heated to temperatures sufficiently high to destroy the more fragile polyatomic molecules. In these warmer regions, smaller molecules such as CO, CH_4, N_2, H_2O and NH_3 could survive and become part of the comet, but the most volatile species (He and H_2) would not condense. This latter situation could correspond to the medium out of which the giant planets were formed and in which molecules such as CH_4 and NH_3 were plainly present.

Although it is evident that there are similarities between interstellar molecules and the molecules in the comae and tails of comets, information is obviously required on the composition of cometary nuclei. Most studies of cometary molecules detect only those species that have travelled a considerable distance from the nucleus and that may be photofragments of larger (parent) species or species formed in chemical reactions in the cometary atmosphere. With such data, one can only deduce the composition of the nucleus by attempting to trace back the processes which lead to the observed species. The true chemical composition of cometary nuclei could be an indicator of the physical and chemical composition of the interstellar or presolar gas from which they are formed; perhaps they will even reveal the composition of the nebula from which the Sun was formed.

In anticipation of data on the true composition of cometary nuclei becoming available, it is clearly of value to appreciate the nature of interstellar molecules, the physical conditions and locations of the clouds where they are detected, their modes of synthesis, their stability and their chemistry. These aspects of interstellar molecules are discussed in the next three sections and, in the final section of this paper, the nature of cometary molecules, as they are presently known (before *Giotto*), and their possible relation to interstellar molecules are discussed.

2. Molecules detected in interstellar clouds and circumstellar shells

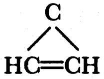
Molecules are observed in various types of interstellar gas clouds, including diffuse clouds and dark and dense clouds, and also in the denser atmospheres of evolved stars (circumstellar shells). The diversity of the molecular species observed in each region reflects the different physical conditions (i.e. gas density, temperature, chemical composition and radiation field) in these various regions. A current list of molecules observed in interstellar and circumstellar regions is given in table 1. They range from the diatomic species such as the ubiquitous H_2, which is by far the most abundant (the next most abundant is CO which is typically 10^4 times less abundant than H_2), to the 13-atomic $HC_{11}N$, which so far has only been detected in the envelope surrounding the carbon-rich star IRC+10216 (Bell *et al.* 1982) and in the Taurus molecular cloud (Bell & Matthews 1985).

Table 1. Molecules detected in interstellar clouds and circumstellar shells

(From various sources including Winnewisser *et al.* (1979), Rydbeck & Hjalmarson (1985), Irvine (1987) and Irvine *et al.* (1986).)

hydrogen H_2

molecules containing only C and H

CH	$C{\equiv}C$	$C{\equiv}CCH$	$(C{\equiv}C)_2H$
CH^+	$C{\equiv}CH$	$H_3CC{\equiv}CH$	$H_3C(C{\equiv}C)_2H$
$^*CH_4$	$^*HC{\equiv}CH$		
	$^*H_2C{=}CH_2$		

molecules containing O

OH	HCO^+	CH_3CHO	CH_3CO_2H
H_2O	HOC^+?	CH_3OH	CH_3OCH_3
CO	H_2CO	CH_3CH_2OH	$HOCO^+$?
HCO	CH_2CO	HCO_2H	$C{\equiv}CCO$

molecules containing N

CN	H_2CN^+	CH_3CH_2CN	$H(C{\equiv}C)_4CN$
HCN	NH_2CN	$H_2C{=}CHCN$	$H(C{\equiv}C)_5CN$
HNC	CH_2NH	$HC{\equiv}CCN$	$C{\equiv}CCN$
N_2H^+	CH_3NH_2	$H(C{\equiv}C)_2CN$	$H_3CC{\equiv}CCN$
NH_3	CH_3CN	$H(C{\equiv}C)_3CN$	$H_3C(C{\equiv}C)_2CN$?

molecules containing O and N

NO, HNO?, HNCO, HOCN?, NH_2CHO

molecules containing S and Si

SO, SN, CS, H_2S, SO_2, OCS, HCS^+, H_2CS, CH_3SH, HNCS, SiO, SiS, $^*SiC_2$, $^*SiH_4$

Molecules marked with an asterisk have been detected only in circumstellar shells. The question marks indicate tentative detections. A tentative detection of NaOH has been reported (Hollis & Rhodes 1982). A detection of HCl has also been reported (Blake *et al.* 1985). $HOCO^+$ and HOCN are both possible assignments for the same lines (Thaddeus *et al.* 1981).

Diffuse clouds are so called because they are partly transparent to visible and ultraviolet radiation ($\lambda > 1216$ Å†), a consequence of the low gas-number densities, which are typically *ca.* 10^2 cm^{-3}. These radiations heat the gas to temperatures that exceed 200 K in some parts of the clouds. It was in diffuse clouds that interstellar molecules (i.e. CH, CH^+, CN) were first detected via their characteristic absorption spectra in the visible region of the spectrum (Swings & Rosenfeld 1937; Dunham & Adams 1937*a*, *b*; McKellar 1941). Only simple (diatomic and triatomic) molecules can exist in significant concentrations in diffuse clouds because the ambient ultraviolet radiation would efficiently photodissociate larger, more weakly bound molecules (van Dishoeck 1986). Detailed atomic and molecular compositions of several diffuse cloud have been obtained. Especially thorough studies have been those of the diffuse clouds in Othe direction of ζ-Ophiucus, χ-Ophiucus, ζ-Perseus and o-Perseus (see van Dishoeck & Black (1986) for details). Typical of the molecules observed in these clouds are HD, OH, CO, CH, CH^+, CN and C_2. The observed relative abundances of these species can be reconciled quite well with relative abundances predicted by gas phase ion chemical models (van Dishoeck & Black 1986), apart from the apparent over-abundance of CH^+ in diffuse clouds. This has been attributed to local shock heating of the gas, which promotes the endothermic reaction of C^+ with H_2 producing CH^+ (Elitzur & Watson (1978); Adams *et al.* (1984*b*) and §3*a*).

A much greater variety of molecular species is observed in the cooler, denser clouds of gas molecules and dust grains, via radio- and millimetre-wave astronomy (Winnewisser *et al.* 1979;

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† Å = 10^{-1} nm = 10^{-10} m.

Guélin 1985; Rydbeck & Hjalmarson 1985). The greater gas-number densities (which can exceed 10^4–10^6 cm^{-3}) and the lower temperatures (lower than 10 K in some clouds) promote the chemistry that results in the generation of complex molecules (see §3*b*). The shielding of these molecules from ultraviolet radiation by the dust grains is essential for their existence. Thus, the wide variety of molecules listed in table 1 (and presumably many more, as yet undetected) can exist in dense and dark clouds among which are the much-studied Orion Molecular Cloud (OMC 1), the Taurus Molecular Cloud (TMC 1) and the giant molecular cloud Sagittarius B2 (Sgr B2). Severe gradients of both gas density and temperature exist in these clouds in which gravitational collapse (clumping) and protostar formation are evident (Evans 1978; Andrew 1980). However, it is clear that, on average, OMC 1 ($T \approx 50$ K) is a somewhat warmer cloud than TMC 1 ($T \approx 10$ K). Also, although many of the molecular species are common to all dense clouds, there are interesting indications of chemical heterogeneity. For example, the clouds in the Taurus region (including TMC 1) are significantly enriched in the cyanopolyyne molecules, HC_nN, compared with other similar regions in the galaxy (e.g. the dark cloud L134N), whereas more C, H, O bearing molecular species have been detected in OMC 1 than in TMC 1 (Irvine 1983). Indeed, it is clear that within some individual clouds there exist spatial variations in the relative abundances of some molecular species. These observations of spatial heterogeneity may be important in the consideration of the origins of comets. This heterogeneity has also attracted the interest of astrochemists and astrophysicists because it raises the question whether differences in molecular composition are due to differences in the elemental composition of the clouds or to the occurrence of a different chemistry involving different rates of chemical evolution under different physical conditions (Penzias 1980; Crutcher & Watson 1985).

The rare stable isotopes of several elements (i.e. D, ^{13}C, ^{15}N, $^{17,18}O$, $^{29,30}Si$ and $^{33,34}S$) have been detected in interstellar molecules. A current list of the rare isotopic variants of interstellar molecules is given in table 2. The abundance ratios of the rare to common isotopic variants of several molecular species have been determined in some interstellar clouds and it is often found that the observed ratios are different from those expected on the basis of terrestrial isotopic ratios. For example, the $^{13}CO/^{12}CO$ ratio in several dense clouds is about twice the terrestrial $^{13}C/^{12}C$ ratio (Winnewisser *et al.* 1979). Also the D/H ratio in interstellar molecules invariably exceeds the terrestrial D/H ratio (Winnewisser *et al.* 1979). Isotopic ratios are of great interest because they can provide an indication of the nuclear history of the galaxy. The D/H ratio is particularly important, not least because it is a critical parameter in cosmological models (Clayton 1985). Because isotopic ratios within the various regions of the galaxy (except for the

TABLE 2. RARE ISOTOPIC VARIANTS OF INTERSTELLAR MOLECULES

(From various sources including Winnewisser *et al.* (1979) and Irvine *et al.* (1986).)

isotope	molecules in which isotope detected
D	H_2, H_2O, HCO^+, N_2H^+, HCN, HNC, NH_3, H_2CO, CH_3OH, HC_3N, HC_5N
^{13}C	CO, CS, HCN, HNC, HCO^+, OCS, H_2CO, HC_3N, CH_3CN, CH_3OH
^{15}N	HCN, HNC, NH_3, N_2H^+
^{17}O	CO, HCO^+
^{18}O	CO, OH, H_2O, HCO^+, H_2CO
^{29}Si	SiO, SiS
^{33}S	CS
^{34}S	CS, SO, SO_2, OCS, SiS

small volume of the interstellar medium near to the Solar System) can only be determined by observing molecular emissions, it is important to appreciate to what extent the isotopic ratios in these molecules are representative of the cloud material as a whole. Careful consideration of this problem, together with the wealth of laboratory data recently obtained on the rates of isotope exchange in ion–molecule reactions, has indicated that enrichment of heavy (rare) isotopes can occur in interstellar molecules as a result of 'isotopic fractionation'. This phenomenon is briefly described in §3*b*.

A rich variety of molecules has also been detected in the atmospheres of envolved stars (notably that of the carbon-rich star IRC+10216, Zuckerman (1980) and Wannier *et al.* (1980)), including many polyatomic species such as the cyanopolyynes. The high pressures and temperatures in the lower atmospheres of such objects ensures that reactions between neutral species are mainly responsible for molecular synthesis, but in the upper atmospheres ionic reactions play an important role (Omont 1987). The first cyclic molecule to be detected in interstellar or circumstellar gas, i.e. SiC_2, was detected in the atmosphere of IRC+10216 (Thaddeus *et al.* 1984), together with the symmetrical molecules CH_4 and SiH_4 (Rydbeck & Hjalmarson 1985), which have not yet been detected in interstellar clouds.

Five molecular positive ions have been identified so far in interstellar clouds (table 1), these being CH^+, HCO^+, N_2H^+, HCS^+ and H_2CN^+. A tentative detection of COH^+ has also been reported, although this identification is unlikely to be confirmed (see §3). A detection of the ion HCO_2^+ has also been reported, but this has not yet been confirmed. However, it is not unreasonable to expect that HCO_2^+ will exist in interstellar clouds, as well as the many other positive ion species that are considered to be involved in the gas-phase ion chemistry leading to many of the observed interstellar molecules.

3. Production of molecules in interstellar clouds

It is now generally accepted that the synthesis of molecules in interstellar clouds occurs largely via gas-phase ionic reactions. Ion–neutral reactions generate complex ions which have to be neutralized to produce the observed wide variety of neutral molecules. The neutralization process is predominantly positive-ion–electron dissociative recombination. Several excellent reviews describe these reaction processes and include many specific examples of reactions that occur in interstellar clouds (Dalgarno & Black 1976; Smith & Adams 1981; Herbst 1985). Production of some molecular species on the surfaces of interstellar dust grains (followed by desorption into the gas phase) cannot be entirely ruled out; indeed, production of the most abundant molecule, H_2, can be quantitatively explained only by invoking grain-surface combination of H atoms followed by desorption. The success of gas-phase ion chemical models in accounting for the relative abundances of most interstellar molecular species is compelling evidence for gas-phase synthesis. Both steady-state (time-independent) and time-dependent models, which involve many hundreds of individual reactions, have been developed to describe the chemical evolution of interstellar molecules (see §3*b*). The central role of gas-phase reactions is also indicated by the apparent enrichment of the rarer (heavy) isotopes in some interstellar molecules. This so-called 'isotopic fractionation' (see, for example, Crutcher & Watson (1985) and also below) is not likely to occur to the extent observed in interstellar molecules if they are formed catalytically on surfaces. However, that both gas phase and to some degree surface production of interstellar molecules occurs is nicely summed up by the phrase often stated by

A. Dalgarno 'The best evidence for grain surface production is the existence of H_2, the best evidence for gas phase synthesis is the abundance of HD'.

Rapid growth in the understanding of interstellar chemistry has taken place during the past few years. The detection of an increasing number of different interstellar molecular species and the determination of their relative abundances has stimulated the development of laboratory experiments to study gas-phase ionic reactions at appropriately low temperatures. As a result, there has been an explosive increase in the amount of kinetic data that are necessary to satisfy the demands of the increasingly sophisticated ion chemical models. The laboratory experiments have also revealed many important routes for the synthesis of interstellar molecules and have indicated important new classes of reactions specific to interstellar chemistry. An example is radiative association (see below). Notable experimental developments have been the variable-temperature selected-ion flow tube (VT-SIFT) experiments (Smith & Adams 1979) which have provided a very great deal of relevant kinetic data (Adams & Smith 1987*a*) and the more recent and very promising CRESU (Cinetique de Reaction en Ecoulement Supersonique Uniforme) experiment, which is now producing kinetic data at temperatures as low as 8 K (Rowe *et al.* 1985). Extensive compilations of the rate coefficients and product-ion distributions for ion–neutral reactions, including many reactions relevant to interstellar and cometary chemistry, have been published (Albritton 1978; Anicich & Huntress 1986). Some recent exciting results, especially those obtained by the VT-SIFT and CRESU experiments, are presented in §4. Important new data are also becoming available relating to the process of dissociative recombination following the development of the flowing afterglow–Langmuir probe (FALP) technique (Adams *et al.* (1984*a*) and see §4).

It is clear that the chemistry occurring in particular interstellar clouds is dependent on the chemical composition and the physical conditions of the clouds. As stated above, it is now known that particular clouds are often very spatially heterogeneous, and much effort is being directed to studying the small-scale variations in composition in particular clouds. More obvious differences are apparent between the types of molecules present in diffuse clouds and in dense clouds, which reflect the obvious differences in the nature of these clouds. Although it is not the intention in this paper to discuss the details of interstellar chemistry, it is instructive to outline the somewhat differing chemistries occurring in diffuse clouds and in dense clouds as these are now understood. Later the elements of cometary chemistry will be discussed.

(*a*) *Diffuse cloud chemistry*

Because of the transparency of diffuse clouds to ultraviolet radiation, which can efficiently dissociate molecules, a substantial fraction of all elements in diffuse clouds exist in the atomic form. Thus the major constituents are H atoms, as well as H_2 molecules, with C, N and O atoms as important minor constituents. These atomic species play a major role in the ion chemistry, via which molecules are synthesized, and this is shown schematically in figure 1. The chemistry is generally considered to be initiated by the ionization of H and H_2 by cosmic rays and by the photoionization of C atoms by ultraviolet radiation. The H^+ and H_2^+ ions so produced then initiate the ionic reactions represented in the upper part of figure 1 and the C^+ primary ion initiates that chemistry represented in the lower part of figure 1. Whereas the chemistry initiated by cosmic rays can occur throughout a diffuse cloud (because of the penetrating power of cosmic rays) the chemistry beginning with C^+ may be more important in the outer part of the cloud where the ultraviolet radiation field is most intense. The chemistry is described by

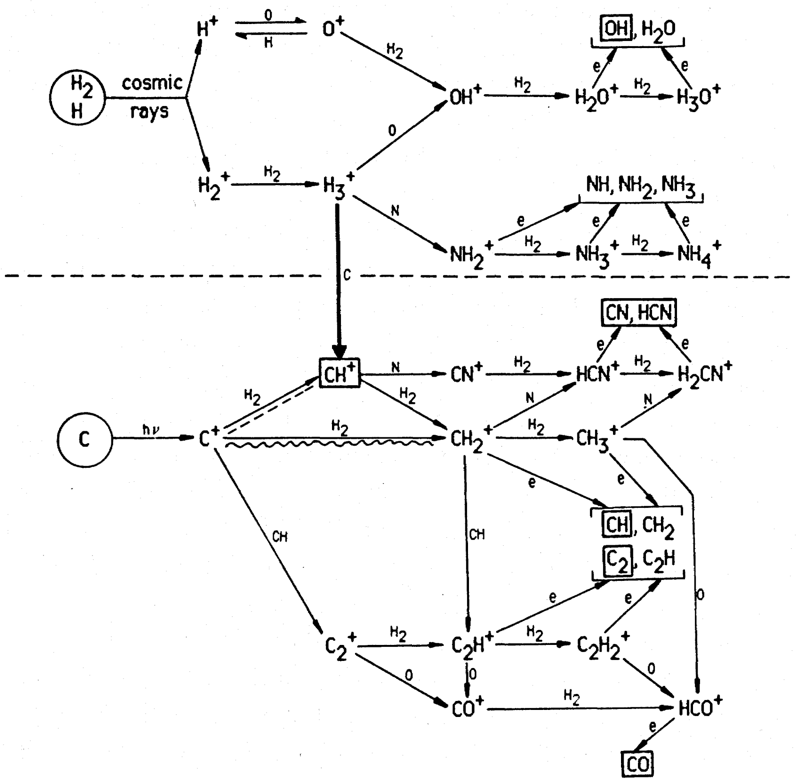

FIGURE 1. A representation of the ion chemistry of diffuse interstellar clouds. The horizontal dashed line divides the chemistry that is initiated by cosmic-ray ionization of H atoms and H_2 molecules from the chemistry that is initiated by ultraviolet photoionization of C atoms. The thick arrow represents the $H_3^+ + C$ reaction which produces CH^+ and which couples these chemistries. The $C^+ + H_2$ reaction, indicated by the dashed line, cannot occur in quiescent clouds and is thought to occur in shocked regions. The $C^+ + H_2$ reaction indicated by the wavy line is a radiative association reaction. The species enclosed by boxes have been positively detected in diffuse clouds. The letter e along an arrow indicates that the ion reacts with electrons undergoing dissociative recombination to generate fragment neutral molecules.

sequences of reactions of ions with atoms (mainly C, N and O) and molecules (mainly H_2 but also small hydrocarbon molecules) generating ions of increasing atomicity which can then react with electrons to produce the fragment neutral molecules shown in figure 1. Again, it is important to note that the concentrations of polyatomic species are limited by photodissociation in the ultraviolet radiation field. Thus, relatively weakly bound species such as NH_3 cannot be present in large concentrations. Note that the ion chemistry leading to nitrogen hydrides shown in figure 1 depends on the reaction of H_3^+ with N atoms which has not yet been observed in laboratory experiments. However, most of the ionic reactions involving H_2, N and O included in figure 1 have been studied experimentally and their rate coefficients measured. A major exception is the very slow, but nevertheless important, radiative association reaction of C^+ with H_2 generating CH_2^+, the rate coefficient for which has had to be obtained by calculation (Black & Dalgarno 1973; Herbst *et al.* 1977). The routes for the production of small hydrocarbon molecules, OH and H_2O and the strongly-bonded CN-bearing molecules and CO are at least qualitatively understood and are as given in figure 1. An important link between the cosmic-ray-initiated chemistry and the ultraviolet-indicated chemistry could be the $H_3^+ + C$ reaction indicated by the thick arrow in figure 1, but this reaction, although expected to be fast, has not yet been studied in the laboratory. The importance of H_3^+ in the ion chemistry of interstellar clouds may be even greater than most models have indicated because of the recent finding that H_3^+ in its ground state does not recombine with electrons (Smith & Adams (1984*b*), Michels & Hobbs (1984) and see §4). Thus the equilibrium concentration of H_3^+ in the clouds will be greater than previously estimated and so its reactions with C, N and O atoms (figure 1) will make a greater contribution to molecular synthesis.

An interesting point to note is the inclusion of the endothermic reaction $C^+ + H_2 \rightarrow CH^+ + H$ in the lower part of figure 1. This reaction cannot occur in quiescent diffuse clouds but can occur in shocked regions where the interaction energy of the C^+ and H_2 is significantly increased (Elitzur & Watson 1978; Draine 1985; Dalgarno 1985). Local shock heating has been invoked to explain the anomolously high abundance of CH^+ observed in diffuse clouds, an abundance which cannot be reconciled with the predictions of models based only on cold chemistry (Adams *et al.* 1984*b*). It is also apparent that figure 1 is a summary only of the ion chemistry and does not involve neutral–neutral reactions which may also contribute to molecular synthesis. For example, the reactions of radicals such as CH and C_2 with O and N atoms could generate the strongly bonded CO and CN molecules and reactions of NH and NH_2 with C atoms could also generate CN radicals. Such neutral reactions would be promoted by the higher temperatures in the shocked regions of interstellar clouds (Dalgarno 1985).

Detailed quantitative models of diffuse cloud chemistry have been produced including those for specific clouds. Very good agreement between observed abundances and those predicted by the models has been obtained for several molecular species (van Dishoeck & Black 1986).

(*b*) *Dense cloud chemistry*

Dense clouds consist largely of H_2 molecules, He atoms and dust grains, the last shielding the central regions of the clouds from stellar ultraviolet radiation, which would effectively dissociate complex molecules. Grains may also play some role in the synthesis of molecules by surface catalysis (Duley & Williams 1984). The ion chemistry is initiated by the action of cosmic rays on H_2 and the He generating H^+, H_2^+ and He^+ ions. As can be seen by comparing figure 1 with figure 2, which is a schematic representation of the ion chemistry of dense clouds, the initial stages of the ion chemistry of dense and diffuse clouds are similar. One difference is that C^+ ions are generated in dense clouds by the reaction of He^+ with the relatively abundant CO rather than by direct photoionization of C atoms. Again, the synthesis of the key molecules H_2O and CH_4 is initiated by reactions of H_3^+ and C^+. It is also possible that NH_3 is generated in dense clouds via the reaction sequence initiated by the H_3^+ reaction with N atoms (see figure 1) as well as by the route shown in figure 2. It is not yet clear which of these two routes predominates. What is more clear (as indicated in figure 2), is the important role of CH_3^+ ions in the chemistry of dense clouds (compared to diffuse clouds). The lower temperatures, higher gas-number densities and the weaker radiation fields in dense clouds promote the production of large molecular ions and hence, via recombination, the production of the observed complex neutral molecules.

To facilitate discussion, the overall ion chemistry represented by figure 2 is roughly divided into left-hand, central and right-hand columns which respectively describe the production of carboxy molecules, hydrocarbon molecules and cyano and amino molecules. The ion species common to each of these chemistries is CH_3^+. This is because, although the reaction of CH_3^+ with H_2 is a vital link in the chain of reactions which generate hydrocarbon molecules, this

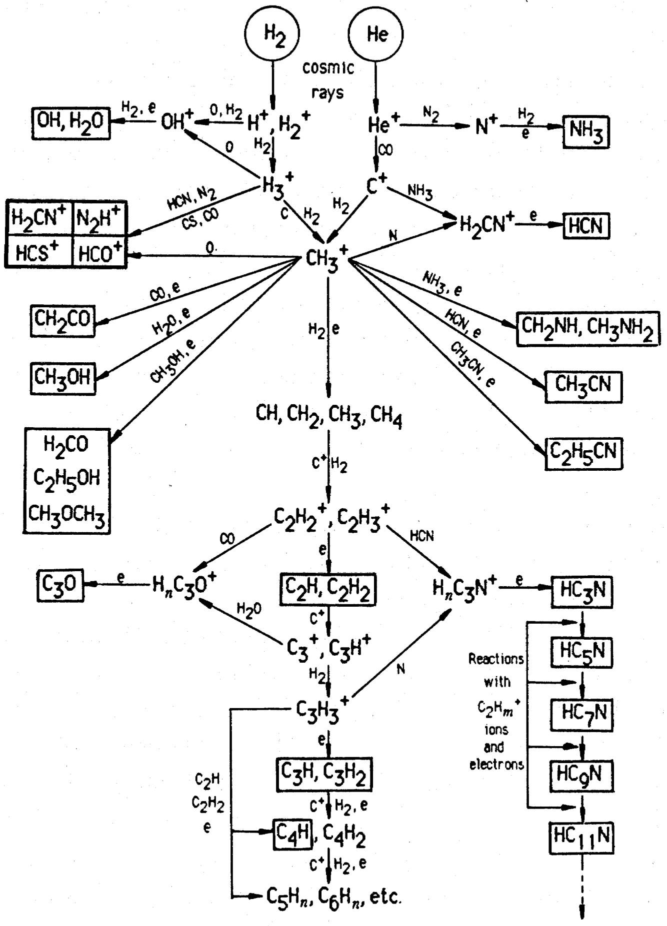

Figure 2. A representation of the ion chemistry of dense interstellar clouds. The ion chemistry is initiated by cosmic-ray ionization of H_2 and He. The production of hydrocarbon molecules is indicated by the central column of the diagram. The production of O-containing and N-containing molecules are indicated in the left-hand and right-hand columns respectively. Where a molecule and an electron lie along an arrow connecting two species, this implies that first an ion–molecule reaction occurs generating a product molecular ion which then undergoes dissociative recombination with electrons to form the neutral molecules indicated. The molecules enclosed by boxes have been detected in dense interstellar clouds. These include the positive-ion species in the thickly lined box.

reaction is relatively slow and therefore some of the CH_3^+ ions can react with minority molecules such as H_2O, NH_3, HCN, etc.

The hydrocarbon reaction chain develops first via the radiative association reaction of CH_3^+ with H_2 (discussed below) which produces CH_5^+ ions. Dissociative recombination of CH_3^+ and CH_5^+ with electrons can then generate small neutral hydrocarbon molecules including CH_4. Reactions of these species with C^+ (and CH_3^+) ions generate ions containing two carbon atoms, reactions known as carbon insertion reactions. Dissociative recombination of the product ions generates C_2H and C_2H_2 molecules. Further carbon insertion reactions generate higher order hydrocarbons as illustrated in figure 2. The $C_3H_3^+$ ions formed in the reaction of C_3H^+ with H_2 are especially interesting because it is likely that a fraction of them are the cyclic isomer and therefore probably the precursor ions of c-C_3H_2, the first cyclic neutral molecule detected in interstellar clouds (Matthews & Irvine (1985) and Thaddeus *et al.* 1985). This is discussed further in §4. Note that the cyclic molecule SiC_2 has only been detected in IRC+10216 (Thaddeus *et al.* 1984).

The cyano and amino molecules (the right-hand column of figure 2), which are so evident in dense interstellar clouds, are largely formed via reactions of hydrocarbon ions with N atoms, NH_3 and HCN. Two possible routes to HCN production are shown in figure 2, these being the reactions of C^+ with NH_3 (which is the most important) and CH_3^+ with N atoms. Reactions of CH_3^+ with NH_3 and HCN followed by dissociative recombination generate the amino molecules CH_2NH and CH_3NH_2 and CH_3CN. Reactions of these product neutral molecules with CH_3^+ can produce higher homologues, for example C_2H_5CN. The well-known interstellar cyanopolyynes, HC_nN, can be produced via the reactions of hydrocarbon ions with both HCN and N atoms as illustrated. Perhaps the more important route to the first of the series, HC_3N, is via the reaction of $C_3H_3^+$ with N atoms (see §4 and Herbst *et al.* 1984*a*). Reactions of HC_3N with hydrocarbon ions can then generate larger molecules in the series, HC_5N, HC_7N, etc. (Knight *et al.* 1986).

The oxygen-bearing molecules are shown in the left-hand column of figure 2. Reactions of CH_3^+ ions are again important; its reaction with CO generates CH_2CO and its reaction with H_2O leads first to the formation of CH_3OH, which may subsequently react with CH_3^+ to produce H_2CO and possibly both of the isomers of C_2H_6O, i.e. C_2H_5OH and CH_3OCH_3. However, it must be stated that an important route to H_2CO could be the neutral–neutral reaction of CH_3 radicals with O atoms (Dalgarno & Black 1976). Higher-order hydrocarbon ions can react with small oxygen-bearing molecules such as CO, H_2O and O_2 generating larger oxygen-bearing molecules. The production of the recently-detected C_3O molecule is an example as shown in figure 2 (Herbst *et al.* 1984*b*).

Four positive molecular ion species HCO^+, N_2H^+, HCS^+ and H_2CH^+ have been detected in dense interstellar clouds and, as shown by the thickly outlined box in figure 2, they are most probably produced in proton transfer reactions of H_3^+ with CO, N_2, CS and HCN. A detection of COH^+ (an isomer of HCO^+) has been tentatively reported (Woods *et al.* 1983), although it is certain that this species cannot be present in appreciable concentrations in dense clouds because it is rapidly converted to HCO^+ in reaction with H_2 (M. J. McEwan 1986 personal communication). Recent work relating to the detection and abundances of HCS^+ and H_2CN^+ is briefly discussed in §4, together with some comments on other sulphur-bearing interstellar molecules that are not included in figure 2 because the routes to their synthesis are uncertain.

Detailed quantitative models of dense clouds (including steady-state and time-dependent models) have been produced involving large numbers of parallel and sequential ionic reactions (see, for example, Millar & Freeman 1984; Leung *et al.* 1984; Millar & Nejad 1985; Millar 1985). Useful review articles are available that describe in detail the gas phase ion chemistry and refer to specific reaction types (Dalgarno & Black 1976; Smith & Adams 1981; Herbst 1985). Some neutral–neutral reactions are included in the models and arguments have been given for grain surface production of some molecules including NH_3 and sulphur-bearing molecules, the production of which cannot yet be convincingly explained via gas phase models of quiescent dense clouds (Millar 1982; Duley & Williams 1984).

It was stated in §2 that the heavy isotopes of some elements were apparently enriched in some interstellar molecules. Deuterium enhancement is particularly obvious. Detailed laboratory studies of isotope exchange in ion–neutral reactions have shown that fractionation of heavy isotopes can occur in these reactions, especially at low temperatures. The elementary reaction

$$D^+ + H_2 \rightleftharpoons H^+ + HD \tag{1}$$

is a good illustration of this phenomenon. As a result of the difference in the zero-point energies of H_2 and HD, (1) is significantly exothermic to the right. Consequently, the endothermic reaction $H^+ + HD$ cannot occur at a significant rate at the low temperatures of interstellar clouds and thus it is expected that much of the deuterium in dense interstellar clouds is contained in HD molecules. Similarly, the reaction

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2 \tag{2}$$

fractionates deuterium into H_2D^+ and subsequent reactions of H_2D^+ with other neutral interstellar molecules, for example, the reaction of H_2D^+ with HCN generating both H_2CN^+ and $HDCN^+$ results in an enhanced abundance of deuterium (relative to hydrogen) in the product molecules. This explains why deuterium is significantly fractionated into DCN relative to HCN. Fractionation of ^{13}C into CO can occur via the reaction

$$^{13}C^+ + {}^{12}CO \rightleftharpoons {}^{12}C^+ + {}^{13}CO \tag{3}$$

and this is probably the reaction responsible for the observed enhanced abundance of ^{13}C in the CO in several dense clouds (Smith & Adams 1980). Detailed laboratory studies of isotope fractionation in ion–neutral reactions have been carried out (Smith & Adams 1984*a*) and the interstellar significance of this phenomenon has also received considerable attention (see, for example, Smith *et al.* (1982) and Crutcher & Watson (1985)). Very recently, following laboratory studies of the reactions

$$C_2H_2^+ + HD \rightleftharpoons C_2HD^+ + H_2, \tag{4}$$

the enhanced abundance of C_2D and the very different C_2D/C_2H abundance ratios observed in OMC 1 and TMC 1 have been explained in terms of the different rates of deuterium fractionation into C_2D (which is formed by dissociative recombination of C_2HD^+ ions) and the temperature dependences of the radiative association rates of $C_2H_2^+$ and C_2HD^+ with H_2 (Herbst *et al.* 1987). It is now clear that isotope fractionation must be taken into account when observed molecular abundances are being exploited, for example, to estimate galactic gradients of isotopic ratios of the elements.

4. Some recent advances in interstellar chemistry

Much of the ion chemistry of diffuse and dense clouds, summarized by figures 1 and 2 respectively, is not contentious, because it has been substantiated both by laboratory studies of many of the reactions and by comprehensive ion–chemical modelling with these laboratory data. However, it is still necessary to make certain assumptions in tracing the synthesis of some observed interstellar molecules which, if shown to be invalid, would require a radical rethink of much of the chemistry. Thus research is proceeding to clarify several aspects of the chemistry, hand-in-hand with more thorough astronomical observations and searches for other interstellar species. Questions being asked include the following. Are the rate coefficients for ionic reactions, which have largely been determined in laboratory experiments at temperatures at 80 K or greater, also appropriate to the lower-temperature conditions of interstellar clouds? How widespread are hydrodynamic and magnetohydrodynamic (MHD) shocks in interstellar clouds and what influence do such shocks have on the chemistry? What is the role of kinetically excited ions? How important is the process of radiative association that is commonly invoked for the synthesis of interstellar molecules? How important are ion–atom reactions and neutral–neutral reactions in the chemistry? What are the products of the dissociative recombination reactions that are so central to current ion–chemical schemes of molecular synthesis? These questions and others are being considered in relation to specific problems such as: the apparent overabundance of HCS^+ and the underabundance of HCl in dense clouds; the unknown routes for the production of cyclic C_3H_2 and the cyanopolyynes; and the recombination rate of the very important H_3^+ ion under interstellar conditions. Some recent progress has been made on each of these fronts and this will now be briefly referred to here.

An important advance has been made recently in the appreciation of interstellar reaction kinetics. Following theoretical predictions (Clary 1985), laboratory experiments have been carried out to measure the rate coefficients for the reactions of ions with polar molecules at low temperatures. These laboratory studies have shown, in accordance with these theoretical predictions, that rapid increases occur in the rate coefficients at low temperatures (Clary *et al.* 1985 and Marquette *et al.* 1985). For reactions involving very polar molecules (such as HCN, HC_3N and CS (see below)), the rate coefficients are more than ten times greater at 10 K than they are at 300 K (Adams *et al.* 1985). This discovery has major implications to model predictions for the rates of production and loss of some interstellar species. An immediate consequence of this work has been to explain the apparently anomalous overabundance of HCS^+ (relative to CS) in dense interstellar clouds (Millar *et al.* 1985). The abundance ratio, HCS^+/CS, predicted by ion–chemical models was a factor of 10–100 lower than the observed abundances, which, unlike the analogous HCO^+/CO ratios, were very variable among interstellar clouds. This worrying problem was resolved by the realization that reactions of the very polar molecule CS proceed much more rapidly than had previously been appreciated and consequently the reassessed production rate of HCS^+ (formed mainly by the reaction of H_3^+ with CS, see figure 2) and the loss rate of CS were both much greater. Following this, the predicted HCS^+/CS abundance ratios now agree with the observed ratios which vary from cloud-to-cloud as a result of the different rate coefficients for the reactions of CS at the different cloud temperatures. The abundance of H_2CN^+ that has recently been detected in Sgr B2 (Ziurys & Turner 1986) is quite consistent with the predicted rapid formation of this ion in the reaction of H_3^+ with HCN (Millar *et al.* 1985).

A great deal of effort is currently being made towards gaining an understanding of molecular synthesis in the shocked regions of interstellar gas. As was previously mentioned (§3*a*), the apparent overabundance of CH^+ in diffuse interstellar clouds has been attributed to shock chemistry (Adams *et al.* 1984*b* and Dalgarno 1985). Efforts have also been made to explain the production of H_2S in an analogous way, i.e. via the sequential reactions

$$S^+ \xrightarrow{H_2} SH^+ \xrightarrow{H_2} SH_2^+ \xrightarrow{H_2} SH_3^+ \xrightarrow{e} H_2S. \tag{5}$$

The three ion–molecule reactions in this sequence are all endothermic and hence cannot occur in cold gas but can occur in shocked gas (Adams *et al.* 1984*b* and Millar *et al.* 1986). Indeed, it has been predicted that the column density of SH^+ ions could be as large as that of CH^+ ions in some MHD shocks although not in purely hydrodynamic shocks. Such an observation could therefore be an important indicator of MHD shocked regions. The influence of kinetic excitation on the rates of some important interstellar reactions, including those leading to the production of NH_3, have been discussed by Adams *et al.* (1984*b*).

As previously stated (§3*b*), and as is clear from figure 2, radiative association is considered to be an important process for the synthesis of many molecules particularly in dense, cold clouds. Yet, until recently, this reaction process had not been observed directly in a laboratory experiment, although there were very strong theoretical and experimental indicators of its importance. However, the radiative association reaction

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu \tag{6}$$

has now been directly observed in the laboratory (Barlow *et al.* 1984). Furthermore, the measured rate coefficient for the binary reaction (6) is in reasonable agreement with that estimated on the basis of the measured rate coefficient for the analogous ternary association reaction

$$CH_3^+ + H_2 + He \rightarrow CH_5^+ + He. \tag{7}$$

This is an important step forward in that the rate coefficients for many of the radiative association reactions included in interstellar ion–chemical models have been derived from their ternary association reaction analogues (Smith & Adams 1978; Herbst *et al.* 1983, 1984*a*). Following this work, it has been reasoned that the cyclic interstellar species c-C_3H_2 is formed in the reaction

$$C_3H^+ + H_2 \rightarrow \text{c-}C_3H_3^+ + h\nu \tag{8}$$

followed by the recombination reaction

$$\text{c-}C_3H_3^+ + e \rightarrow \text{c-}C_3H_2 + H. \tag{9}$$

Although further work is required before this can be confirmed, it has been shown (Adams & Smith 1987*b*) that the ternary analogue of (8) does result in the production of c-$C_3H_3^+$. However, whether (9) results in the production of c-C_3H_2 remains to be determined.

Radiative association has also been invoked to explain the production of the cyanopolyyne series of molecules (Herbst *et al.* 1984*a* and Knight *et al.* 1986). As stated above, the production of the first of the series, HC_3N, probably proceeds via the recently studied reaction (Federer *et al.* 1986)

$$C_3H_3^+ + N \rightarrow H_2C_3N^+ + H \tag{10}$$

followed by the recombination reaction $H_2C_3N^+ + e \rightarrow HC_3N$. (Atom reactions are technically more difficult to study than reactions with stable molecules but important developments in technique are facilitating such studies (Adams & Smith 1985; Federer *et al.* 1986.)) An extensive study of the reactions of HC_3N has been carried out recently and reactions of the type

$$C_2H_2^+ + HC_3N + He \rightarrow H_3C_5N^+ + He \tag{11}$$

have been observed (Knight *et al.* 1985). It has also been postulated that other members at the cyanopolyyne series may be synthesized in interstellar clouds by radiative association analogues of reactions such as (11) (Schiff & Bohme 1979; Knight *et al.* 1985*b*).

Concerning dissociative recombination reactions of interstellar ions, a recent result worthy of note is the finding that the major interstellar ion H_3^+ (when in its ground state) does not recombine with electrons at a significant rate (Adams *et al.* 1984*a*; Michels & Hobbs 1984). The implications of this to interstellar physics and chemistry have been discussed recently (Smith & Adams 1984*b*). Work has also begun to determine the neutral products of dissociative recombination reactions of interstellar ions (Quéffelec *et al.* 1985; Vallée *et al.* 1985).

5. Cometary molecules and cometary chemistry

Molecules are observed in both the comae and the tails of comets and include several ionic species. A list of the atomic and molecular species so far observed in cometary atmospheres is given in table 3. Some of the species in the list are rather recent, somewhat tentative identifications. Compared to interstellar molecules, there is a preponderance of diatomic and triatomic species including several radical species which are probably fragments of more stable parent molecules that have sublimed from the cometary nuclei. Primary ions are formed by the action of solar photons and the solar wind on these molecules. Other ions can be formed by ion–molecule reactions (see below). Some cometary molecules have not been observed in interstellar clouds, including NH and NH_2, which are presumably photofragments of NH_3 parent molecules. The important question to be answered is, given the relative concentrations of the observed species in the comae and/or the tails, can the nature of the material in the nuclei be deduced? To answer this question requires a great deal of information including the rate coefficients for many chemical reactions and the photodissociation and photoionization cross sections for many species over the broad wavelength range of the solar spectrum (Oppenheimer 1975; Huntress *et al.* 1980; Lüst 1981; Mitchell *et al.* 1981; Biermann *et al.* 1982; Huebner 1985). The lack of data on the latter process is particularly frustrating to progress (van Dishoeck 1987). Concerning the chemistry, a good deal of ionic reaction rate data are available but kinetic data on relevant radical–radical reactions are much more scarce. Thus, the quantitative aspects of cometary chemistry are not very advanced.

Table 3. Atomic and molecular species observed in cometary atmospheres

(List compiled from various sources including Lüst (1981) and Irvine *et al.* (1986).)

C and H species

H, C, C^+, CH, CH^+, C_2, C_3

species containing O

O, OH, OH^+, H_2O?, H_2O^+, CO, CO^+, HCO, CO_2^+

species containing N

NH, NH_2, NH_3?, N_2^+, CN, CN^+, HCN?, CH_3CN?, HC_3N?

S and Si species

S, SH^+, H_2S^+, CS, CS^+, S_2, Si

metals

Na, K, Ca, Ca^+, Y, Cr, Mn, Fe, Co, Ni, Cu

The question marks indicate tentative detections.

Figure 3 is a schematic representation of some of the likely ionic reactions occurring in cometary atmospheres. It is constructed on the assumption that the parent molecules originating from the nucleus are H_2O, CO_2, NH_3, CH_4 and H_2S, that is the kind of species that are expected to be present in the presolar nebula. The primary processes are largely photodissociation and photoionization which result in fragment radicals and ions. As can be seen in figure 3,

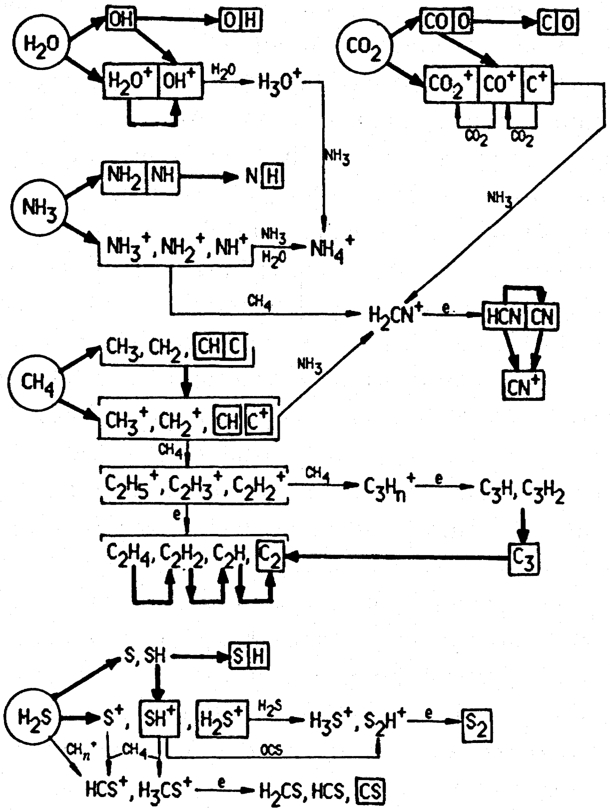

Figure 3. A representation of some of the routes to the production of some observed cometary species (which are enclosed in boxes). It is assumed that the species enclosed by circles are subliming from the cometary nucleus. The thick arrows indicate photodissociation and photoionozation. Thus, for example, H_2O can be photodissociated to OH or photoionized to H_2O^+ and OH^+. The thin arrows indicate ion–neutral reactions and e above the arrows signifies dissociative recombination leading to the indicated neutral molecules. Note the coupling of the NH_3, CH_4 and CO_2 chemistries which produce HCN. Other couplings must occur but are not represented here.

many of the species actually detected in cometary atmospheres can be produced by photofragmentation of these assumed parent molecules. Other observed species can be produced via gas phase ionic reactions similar to those discussed previously in the context of diffuse and dense interstellar cloud chemistry. A detailed discussion of the ion chemistry is unwarranted here, but a few comments are in order.

The ion chemistries of the species derived from H_2O, CO_2 and NH_3 are straightforward (see figure 3). The chemistry of methane-derived species is similar to that occurring in dense clouds but, because of photofragmentation, more radical species are probably involved. Significant in this chemistry is the production of C_2 and C_3 molecules which are both observed in comets. (C_3 has not yet been detected in interstellar clouds.) If $C_3H_n^+$ ions are formed in reactions of $C_2H_n^+$ ions with hydrocarbons and if C_2 and C_3 molecules are formed by dissociative recombination of $C_2H_n^+$ and $C_3H_n^+$ ions, then it is reasonable to expect that C_2 would be present in greater concentration than C_3 because of the additional reaction step required to produce C_3. That the reverse is so casts some doubt on the production scheme outlined in figure 3 for C_2 and C_3. However, without detailed quantitative modelling which must include reliable photodissociation crosssections, this is not yet a convincing argument against this reaction scheme. It has, however, prompted the suggestion (A. Dalgarno 1986 personal communication) that C_3 may originate from photofragmentation of C_3H_2 (the known cyclic interstellar molecule) or other organic molecules may be subliming from cometary nuclei. C_2 is then generated by further photofragmentation of the C_3. Alternatively both C_2 and C_3 may be sputtered from cometary grains. The relatively large concentration of C_3 relative to C_2 is perhaps a strong argument for the interstellar origin of comets. Perhaps the *in situ* observations from the *Giotto* instruments might cast some light on this problem.

The sulphur chemistry outlined in figure 3, describing the production of S_2 and CS molecules which are both observed in cometary atmospheres, requires a substantial concentration of H_2S to be present in the cometary atmosphere to drive the chemistry rapidly because S_2 is detected only near the nucleus. If this chemistry is too slow to produce sufficient S_2 then the inevitable conclusion has to be drawn that the S_2 is subliming from the nucleus. However, the production rate of S_2 is considerably enhanced if it can be assumed that OCS is available in significant concentrations and this is included in the scheme for S_2 production in figure 3. As in the discussions of interstellar chemistry, neutral–neutral reactions have not been included in figure 3, but such are possible in cometary atmospheres. For example, the reaction of NH radicals with C atoms could generate CN radicals which are so evident in comets.

Finally, as has been mentioned above (§§2 and 3*b*), great interest has centred around isotopic ratios in interstellar gas as tracers of the nuclear history of the galaxy. Similarly, the isotopic ratios in cometary material, particularly the D/H ratio, could be an indicator of the origins of comets. It is hoped that the *Giotto* mission and future cometary missions might provide accurate isotopic ratios for some elements.

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Discussion

M. K. Wallis (*Department of Applied Mathematics and Astronomy, University College Cardiff, U.K.*). Extending Professor Anders's point, detailed modelling by Mitchell *et al.* and Huebner *et al.* (1982) has shown that sufficient complex molecules cannot be built up in cometary atmospheres, for time is too short in the expanding coma for equilibrium chemical thermodynamics to apply. The icy-clathrate hypothesis (Delsemme & Swings 1958) that supposes the nucleus is composed of ices of simple gases, has failed; in particular the fraction of NH_3 must be low to permit the observed H_2O ions. The long-observed C_3 and recent S_2 compounds must derive by breakdown of complex parents. My question is, might interstellar molecules give the sulphur dimer S_2, or must it be of mineral origin?

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D. Smith. S_2 molecules can be synthesized in intersteller clouds via ion–molecule reactions (producing S_2H^+) followed by proton transfer (e.g. $S_2H^+ + NH_3 \rightarrow S_2 + NH_4^+$) or dissociative recombination ($S_2H^+ + e \rightarrow S_2 + H$). Therefore S_2 could be present in cometary nuclei perhaps in the form of $(S_2)_n$ oligomers which can then sublime into the comae to be dissociated to the observed S_2 molecules.

F. L. Whipple (*Smithsonian Astrophysical Observatory, Cambridge, Massachusetts, U.S.A.*). I wonder how stable Dr Kroto's C_{60} molecules would be in the interstellar medium or the solar nebulae under the conditions in which comets may have formed.

D. Smith. In Kroto's laboratory experiments, the C_{60} molecules are ejected from a solid surface by a pulse of laser light. I would guess, therefore that C_{60} would be stable in cold interstellar clouds or in the cooler regions of the presolar nebula.