old these objects are, however they do appear to be at least 10^7 years old (Cohen *et al.*, 1979) and perhaps even older (Solomon and Sanders, 1979; Solomon, Scoville and Sanders, 1980). The Columbia studies indicate that the GMCs congregate mainly in the spiral arms but in the other study this is not so obvious. The surveys indicate that CO is taking over from the H 21 cm line as the major probe of galactic structure. The future task of mapping the Galaxy in CO and determining the relationships between large and small scale studies is the most important in galactic astronomy.

Comets

Similar types of molecule to those observed in the ISM have been detected in comets. The identification by Douglas (1951) of C_3 seems to fit rather neatly with the recent detection of carbon chain molecules. Ions and radicals have been identified and most interestingly so too has the ion H_2O^+ by Wehinger *et al.* (1974). This detection may be an indicator that icy water particles are a major component of the comet's structure. A short recent review of the chemistry of comets has been given by Oppenheimer (1980).

These objects demand further attention because they may well be test tube samples of the ISM brought directly to our doorsteps for analysis. We tend to think of comets as individual objects but it is possible that large clouds of comet-type objects exist which emit radio waves and it could be difficult to show that the cloud has such an inhomogeneous microstructure. Certainly the rôle of comet-size objects in the formation of stars and planets is not understood and it is possible that such objects form at some important phase of cloud collapse.

So far the molecules CH, CH^+, CN, C_2, C_3, CO, CO^+, CO_2^+, CS, OH, OH^+, H_2O^+, NH, NH_2, HCN, CH_3CN and N_2^+ have been detected in comets.

INTERSTELLAR CHEMISTRY

Ever since the detection of CH, CH^+ and CN the problem of how such molecules could be formed and survive in the ISM has been a field for study. The detections of OH and the further molecules detected since 1968 (*see* Table 1) have injected the study of interstellar chemistry with a new lease of life. It is not at all clear at this moment that we really understand the problem. New discoveries always seem to chip away at the confidence previously placed in a particular scheme. A general review has been presented by Watson (1976).

There are three main theories each with adherents who cling (like all true believers) with grim attachment to their own particular credo. The three main processes are:

1. Reactions on grain surfaces.
2. 2-Body gas phase ion molecule reactions.
3. Circumstellar shell formation followed by ejection into the ISM.

Of course all three may be important in general and one may be more or less important in one part of the ISM than another. The balance is certainly not at all clear.

In general two colliding atoms (i.e. two H atoms) cannot stick together unless the excess kinetic energy is taken away by a third body. This may be a simultaneously colliding third body, an emitted photon or an electron. The first process is governed by the 3-body collision lifetime

$$\tau_{3b} = {\sim}3 \times 10^{23}/n^2 \text{ years} \qquad (28)$$

where n is the number density of the ISM, which in the denser regions is mainly H_2. Even in the denser regions where $n \sim 10^6\,\mathrm{cm}^{-3}$ it takes a bit too long for even one 3-body collision to take place as the Universe is only $\sim 1.5 \times 10^{10}$ years old.

The second process requires a photon to be emitted during a vibrational period ($\sim 10^{-13}$ s). For an allowed infrared transition $\tau_{ir} \sim 10^{-7}$ s and so the lifetime for radiative association is

$$\tau_{ra} \sim 10^9/n \text{ years} \tag{29}$$

The third process is discussed further below.

The big problem is to find a way for H_2 molecules to form in the first place. They cannot form by radiative association as only *quadrupole* emission, which is very weak, is allowed. The most favoured mechanism for forming H_2 is the grain surface catalysed reaction (McCrea and McNally, 1960)

$$\mathrm{H} + \mathrm{Gr} \longrightarrow \mathrm{H} \cdots \mathrm{Gr}\ \mathrm{H} \xrightarrow{\mathrm{H}} \mathrm{H} \cdots \mathrm{Gr} \cdots \mathrm{H} \longrightarrow \mathrm{Gr} \cdots \mathrm{H}_2 \longrightarrow \mathrm{Gr} + \mathrm{H}_2$$

The hydrogen attaches by weak forces to the grain surface at a rate (Watson, 1976)

$$\tau_g \sim 10^9/n \text{ years} \tag{30}$$

after which it tunnels about until it reacts with a second H atom forming H_2 which then detatches. Though H_2 can be detatched at low temperatures $\sim$ 10 K it is not clear whether other molecules can get off very easily. CO and N_2 may evaporate but many of the recently detected species such as CH_3CH_2OH or even H_2O might have very great difficulty.

As far as grain chemistry in general is concerned the unknown surface composition is a major problem. Indeed it is fair to say that little if anything is known about their chemical composition. Laboratory investigations which should shed light on this field are being pursued (Hagen, Allamandola and Greenberg, 1979; Greenberg, 1975). It is possible that some chemical mechanisms such as exothermic bond formation may heat up small grains sufficiently for molecules to evaporate or cause localised heating of larger grains. It is also possible that photons and X or cosmic rays or electrons may heat the area where the molecule is attached sufficiently to cause it to unstick.

A large number of possible grain surface reactions have been discussed by Allen and Robinson (1977) as possible routes to interstellar species.

Exothermic gas-phase ion–molecule reactions, many of which have zero activation energies and large reaction cross-sections, offer particularly attractive routes to interstellar molecules. There are several major reviews highlighting various aspects of the chemistry in detail. Solomon and Klemperer (1972), Dalgarno and Black (1976) and Dalgarno (1976) have discussed the chemistry of diffuse clouds, Herbst and Klemperer (1973) that of dense clouds. There are also useful reviews by Huntress (1977), McDaniel *et al.* (1976), Watson (1977, 1978) and in this issue by Smith and Adams (1981).

The ionization of species such as H, H_2 and He by photons in diffuse clouds and cosmic rays in dense clouds is passed on to less abundant atoms such as O, etc, by chains of 2-body transfer reactions which in turn lead to some of the small polyatomic molecules detected in the ISM. Such processes can proceed at the Langevin rate, (Gioumousis and Stevenson, 1958), i.e. at every ion-molecule collision.

A typical example of a chain that can occur in a dense cloud is

$$\mathrm{H}_2 \xrightarrow{\text{c.r.}} \underset{+e^-}{\mathrm{H}_2^+} \xrightarrow{\mathrm{H}_2} \underset{+\mathrm{H}}{\mathrm{H}_3^+} \xrightarrow{\mathrm{CO}} \underset{+\mathrm{H}_2}{\mathrm{HCO}^+}$$

for which Herbst and Klemperer (1973) obtain a time to reach steady state abundance $n_{\mathrm{HCO^+}} \sim 10^{-4}$ cm^{-3} of $\sim 10^3$ years. There are of course a myriad of similar chains which may be invoked to synthesize other species. For instance H_2O may be formed via a sequence such as

$$\begin{array}{ccccccccccccc} \mathrm{He} & \xrightarrow{\text{c.r.}} & \mathrm{He}^+ & \xrightarrow{\mathrm{O}} & \mathrm{O}^+ & \xrightarrow{\mathrm{H_2}} & \mathrm{OH}^+ & \xrightarrow{\mathrm{H_2}} & \mathrm{OH}_2^+ & \xrightarrow{\mathrm{H_2}} & \mathrm{OH}_3^+ & \xrightarrow{e^-} & \mathrm{OH}_2 \\ & & +\mathrm{e} & & +\mathrm{He} & & +\mathrm{H} & & +\mathrm{H} & & +\mathrm{H} & & +\mathrm{H} \\ & (a) & & (b) & & (c) & & (c) & & (c) & & (d) & \end{array}$$

which involves

(a) cosmic ray ionization
(b) electron transfer
(c) three exchange reactions
(d) a final dissociative e$^-$/ion recombination.

Clearly the reactions in diffuse clouds are governed by the different overall physical conditions. In the diffuse clouds photons as well as cosmic rays can penetrate and inject the energy which is converted to chemical energy. However, these are relatively unshielded regions and so some form of kinetic balance is set up between the formation and photodissociation processes which allows only the smaller (mainly diatomic) and less readily dissociated species such as CO to survive and build up in significant concentrations.

In the denser clouds only high energy cosmic rays can penetrate and inject the requisite energy and once formed the molecules are so well protected by their grain colleagues that they will last indefinitely. It is probably pitch black inside the clouds and pitch may not be a metaphor.

The quantitative studies indicate that the smaller molecules, involving 2–4 atoms can be formed at reasonable rates. Species such as CH may be formed via radiative association steps such as

$$\begin{array}{ccccc} \mathrm{C}^+ & \xrightarrow{\mathrm{H_2}} & \mathrm{CH}_2^+ & \xrightarrow{e^-} & \mathrm{CH} \\ & & +h\nu & & +\mathrm{H} \end{array}$$

However the H_2, needed to form CH, tends to destroy CH$^+$ (via: $\mathrm{CH^+} + \mathrm{H_2} \rightarrow \mathrm{CH_2^+} + \mathrm{H}$) and so the abundance of CH$^+$ is still a problem (Dalgarno, 1976). This problem was the first one tackled by Bates and Spitzer (1951) in their pioneering study in interstellar chemistry.

Apart from the fact that many of the small molecules can be accounted for by these processes the observation of HCO$^+$, $\mathrm{HN_2^+}$ and HNC are rather convincing indicators that these reactions are significant. In addition the departure of the apparent interstellar isotope ratios from the cosmic ratios seems to be nicely explained by ion-molecule isotope fractionation. Isotope ratios of $\sim 1/40$ for ^{12}CO/^{13}CO as compared with the terrestrial ratio of 1/89 have been observed. In the case of D/H as observed in HCN/DCN by Wilson *et al.* (1973) the effect is much larger $\sim 1/100$ as compared with the cosmic value of $\sim 1/10^4$. These effects can be explained by taking into account the exothermicity of exchange reactions such as

$$^{13}\mathrm{C}^+ + {}^{12}\mathrm{CO} \rightleftarrows {}^{13}\mathrm{CO} + {}^{12}\mathrm{C}^+ + \Delta\mathrm{H}.$$

ΔH is readily determined from the change in the zero point energy ($^{12}\mathrm{CO} \rightarrow {}^{13}\mathrm{CO}$) which is essentially due to the reduced mass dependence of the vibrational frequency. As

$\omega(^{12}CO) = 2143$ and $\omega(^{13}CO) = 2095$ cm^{-1} $\therefore$ $\Delta H = 24$ cm^{-1}. The equilibrium constant for this process at 80 K has been determined by Smith and Adams (1980) and it fits in beautifully with this simple theory and neatly explains the observed $^{12}CO/^{13}CO$ abundances.

The explanation of anomalous isotopic abundances by fractionation is a very strong argument in favour of ion–molecule reactions. These fit nicely as they are fast at the low temperatures as they have negligible activation energies in general. For higher temperature reactions isotope fractionation should be negligible.

Smith and Adams (1977) have determined many of the rate constants required for a detailed analysis of ion–molecule chemistry using the SIFT technique (*see* review in this issue). Huntress (1977) had discussed complementary data obtained using the ICR (ion cyclotron resonance) technique. The effective temperatures of the reactants in the ICR method may be quite high and thus the data may not apply directly to the low temperature ISM.

Prasad and Huntress (1980) have recently presented the results of a very large computer study of the chemistry of the ISM. It is still not at all obvious how molecules such as HC_9N can be produced in cold clouds by a sequence of two-body coupling reactions. Schiff and Bohme (1980) have suggested a possible sequence of steps. It may be that radiative association and neutral–neutral processes may become significantly more important for larger molecules.

The third process which must be taken very seriously is that of molecule formation in high temperature, high density, circumstellar envelopes followed by their subsequent ejection into the general ISM. This mechanism is further discussed in the last section.

DISCUSSION

It would be remarkable if radio spectroscopy were to continue to spring as many exciting surprises in the next decade as it has in the last, but of course this is possible. There are a few areas which can be identified as requiring major efforts in development. New laboratory techniques for producing astrophysically important microwave and infrared spectra are needed. The spectra of free radicals, molecular ions (positive and negative), unstable molecules with multiple bonds and second row atoms are particularly important. More work on high temperature species is also necessary. In addition collisional and radiative energy transfer processes are important and as higher temperature regions are probed, vibrational satellites are becoming detectable. Certainly a great deal of effort is being put into the solution of some of these problems as discussed below.

Obviously one must always strive for higher sensitivity, speed of data collection, spatial resolution, etc. and as successive advances are made some of the goals will hopefully be achieved and new, unexpected discoveries will be made. The most recent high resolution surveys are indicating that the interstellar radio spectrum appears to be rather cluttered up at least at mm wave frequencies. It is now becoming clear that we have only identified the sparse long grass and there may well be a rather dense undergrowth of weak lines which will be difficult to disentangle. Much greater sensitivity may just uncover myriads of weak lines offering few prospects for certain identification. There may thus be a limit to the number of molecules that can be identified by radio techniques (~150?).

In the infrared range the problem may be more serious as each vibrational band is accompanied by an entourage of complicated rotational branch structure which will limit the value of the technique for the study of larger molecules.

The study of interstellar molecules is an expanding field, expanding in many directions and the rest of this section is devoted to a review of some of the important questions which