We discuss several types of regions in the interstellar medium of the Milky Way and other galaxies in which the chemistry appears to be influenced or dominated by surface and solid-state processes occurring on or in interstellar dust grains. For some of these processes, for example, the formation of H₂ molecules, detailed experimental and theoretical approaches have provided excellent fundamental data for incorporation into astrochemical models. In other cases, there is an astrochemical requirement for much more laboratory and computational study, and we highlight these needs in our description. Nevertheless, in spite of the limitations of the data, it is possible to infer from astrochemical modelling that surface and solid-state processes play a crucial role in astronomical chemistry from early epochs of the Universe up to the present day.

1. Introduction

Optical absorption spectra believed to be from molecules in the diffuse interstellar medium were first obtained in 1937 and by 1941 had been attributed to CH, CH⁺ and CN [1–5]. These assignments were, at the time, considered remarkable because the diffuse interstellar medium had long been held to be a hostile environment for molecules [6]. Various attempts were made to understand how these molecules could be formed efficiently in the diffuse interstellar medium, the most comprehensive investigation being that of Bates & Spitzer [7]. Those authors introduced all the many types of gas-phase reactions currently invoked in interstellar chemistry, but were forced to consider the possibility that chemical reactions at the surfaces of dust grains may also play an important part.
Following the exploration by Bates & Spitzer of the possible chemical pathways, simple networks of gas-phase reactions were investigated by various authors in attempts to explain the origin of the detected interstellar species (including OH, after its discovery in the radio spectrum in 1963 [8]). These networks assumed the existence of interstellar molecular hydrogen as an essential chemical partner, even though H₂ was not identified in the interstellar medium until 1967 [9] through its Lyman and Werner band absorptions in a rocket-borne UV experiment. Molecular hydrogen was considered to be important because it was believed (correctly) likely to have a high abundance in interstellar clouds. However, it was accepted very early on that H₂ was probably formed at the surfaces of interstellar dust; gas-phase reactions forming H₂ under interstellar conditions of the Milky Way Galaxy were known to be too slow to compete with photodissociation [10], so surface reactions were invoked by default. Consequently, the theoretical study of surface reactions in the interstellar medium to form H₂ and other species began to be investigated in detail in the 1960s [11,12]. Thus, surface science in the interstellar medium has been a topic of continuing interest for half a century. However, laboratory studies of these processes had to wait until techniques improved sufficiently to be able to approach the physical conditions of interstellar space, some three decades later. The composition of the dust on whose surfaces the reactions occur remains to some extent uncertain; however, it is clear that one important component of the dust is amorphous silicate, and another is carbonaceous material, possibly graphitic but without long range order; there may also be free-flying polycyclic aromatic hydrocarbons containing less than 100 carbon atoms, but with graphitic (sp² valence) structure [13,14].

From the 1970s onwards, improvements in detector technology at infrared, millimetre and submillimetre wavebands enabled a flood of identifications of relatively complex interstellar molecular species to be made. The number of molecular species identified in the interstellar medium—not counting isotopologues—currently stands at around 170, and if isotopologues are included, the number is several times larger (http://www.astro.uni-koeln.de/cdms/molecules/; http://www.astrochymist.org/astrochymist_ism.html).

Our knowledge of the structure of the interstellar medium was greatly broadened by the detection of interstellar molecules. Most importantly, observations of CO emission in its rotational transitions revealed the existence of giant molecular clouds containing condensations that are very much denser and colder than gas in the diffuse interstellar medium. Infrared studies of these condensations showed absorptions corresponding to solid-state molecules, and it was realized that molecules could freeze out on dust grain surfaces. Indeed, it was apparent at an early stage that the existence of these ices implied that chemical reactions were occurring in and on the ices to form the major component, water ice [15]. Detailed modelling, as well as gas-phase experiments [16], revealed that species such as methanol and formaldehyde could not be produced in gas-phase reactions in the abundances observed in the ices, and chemical processing of CO within the ices was invoked, which was supported by laboratory studies [17,18]. The detections in some locations of relatively large molecules (e.g. methyl formate, glycolaldehyde, etc.) [19] have emphasized the failure of purely gas-phase chemistries to produce the observed variety and abundances of species. It is now accepted that chemical processing of interstellar ices is an important component of astrochemistry, along with surface reactions on dust grains, and that these processes must interact with a large and complex network of gas-phase reactions.

We work as modellers of interstellar physics and chemistry. Our aim is to use observations of molecules as tracers of the physical conditions in the interstellar media in the Milky Way and external galaxies, to infer using our models the current physical state and probable evolution of these regions, and to understand better the formation of stars and galaxies from interstellar matter. Our models rely on a vast amount of data for gas-phase, surface and solid-state chemistry. Databases listing relevant reaction rate data are available (www.udfa.net; www.physics.ohio-state.edu/~eric/research.html; kida.obs.u-bordeaux1.fr), and the value of our conclusions depends heavily on the accuracy of the chemical data incorporated into our models. While the situation is clearly very much better than half a century ago and some major...
uncertainties have been removed, other data remain poorly known. We review here uncertainties in surface and solid-state data for a variety of interstellar regions in the Milky Way and external galaxies in which surface and solid-state chemistry is believed to play a role.

2. Interstellar diffuse clouds

(a) Molecular hydrogen

Diffuse clouds are low density (number density of H atoms in all forms, \( n_H \), typically approx. 100 cm\(^{-3}\)), cool (kinetic temperature, \( T_K \), typically approx. 100 K) and reasonably transparent to optical starlight (optical depth in the visual (555 nm) \( \leq 1 \)). They contain a variety of (mainly diatomic) molecules, produced in a reasonably well-determined network of gas-phase reactions (though a couple of anomalies require explanation by invoking special physical conditions). This gas-phase chemistry relies wholly on the presence of \( \text{H}_2 \) (and is energized by UV starlight and by cosmic rays (mainly approx. 10–100 MeV protons)). The essential point is that hydrogen molecules cannot be formed in diffuse clouds at a high enough rate in gas-phase reactions to counter photodestruction by starlight, and it has been inferred that \( \text{H}_2 \) is formed in reactions at the surfaces of dust grains. This conclusion is now confirmed by detailed theoretical and experimental studies. Thus, all of diffuse cloud chemistry (and much of the chemistry in other regions) depends ultimately on the surface processes that form \( \text{H}_2 \). This surface reaction is, therefore, of fundamental importance for all of cosmic chemistry.

Experiments on the formation of HD molecules under conditions approaching interstellar have been performed for a variety of dust grain surfaces in various laboratories, including those in Syracuse, NY [20,21], London [22,23] and Paris [24]. These show that within a particular range of surface temperatures, the reaction is efficient, occurring at almost every collision on the plausible surfaces of carbons and silicates. This characteristic behaviour is supported by \textit{ab initio} theoretical studies at London, Oxford and Sheffield [25]. Recent work [26] shows that the rather narrow range of temperature for efficient \( \text{H}_2 \) formation found in early work is in fact wider than previously measured, and this effect is attributed to a combination of Langmuir–Hinshelwood and ‘hot atom’ diffusion of surface atoms. Chemisorption sites may also be involved.

When the data from these experiments on HD formation are directly applied to the interstellar case and combined with the accepted dust size distribution and the gas kinetic temperature, the computed overall \( \text{H}_2 \) formation rate is generally sufficient to sustain the observed \( \text{H}_2 \) abundance against photodestruction by the interstellar radiation field. Each line of sight through the interstellar medium is, however, different in terms of gas number density and temperature, and radiation field.

The London experiments measure the internal and kinetic excitation of the nascent \( \text{H}_2 \), and the energy deposited in the dust at each \( \text{H}_2 \) formation. All these quantities are important in the energy budgets of the interstellar medium, and particularly for transient heating of dust.

We conclude that \( \text{H}_2 \) formation on model dust surfaces is well constrained by experiment and theory, and that the implications for \( \text{H}_2 \) formation in the interstellar medium are probably consistent with the observational constraints.

(b) Other reactions on dust

Evidently, the surfaces of dust grains are chemically reactive. Do other relatively abundant species in diffuse clouds, for example, \( \text{C}^+ \), O, N, also react? If so, given the preponderance of hydrogen, the products will be hydrogenated forms of these species.

The species \( \text{NH} \), \( \text{NH}_2 \) and \( \text{NH}_3 \) have been detected on diffuse lines of sight by the Herschel space observatory [27]. Gas-phase routes to these species are controversial, but we have shown that an assumed reaction involving efficient hydrogenation of nitrogen at surfaces could readily account for the NH abundance without adverse chemical consequences [28]. However, no
laboratory studies of this surface reaction to test this scenario have yet been made under conditions approaching those in diffuse interstellar clouds.

Herschel detections of OH$^+$, H$_2$O$^+$ and H$_3$O$^+$ in diffuse clouds have also been made [29]. Conventional ion–molecule gas-phase chemistry involving O$^+$ ions appears capable of accounting for the observed abundances of these species. However, it is unclear what happens when neutral O atoms encounter a dust grain surface in the hydrogen-rich diffuse interstellar medium. Observations of denser, darker regions imply that water is formed and at least some of it retained at the surface (see §3a). In the warmer, more strongly irradiated diffuse medium, it may be that any H$_2$O formed is ejected to the gas. Our modelling studies [30] show that this additional source of H$_2$O would not conflict with observational data. However, there are no laboratory studies appropriate to interstellar conditions of the interaction of O atoms with model dust surfaces.

Carbon is also abundant in the diffuse interstellar medium. Many plasma experiments suggest that carbon in a hydrogen atmosphere is deposited on cold surfaces as sp$^3$ (polymeric) carbon, and that it may subsequently be annealed by UV to sp$^2$ (graphitic form). This suggests that some of the interstellar silicate dust may be coated with carbon [31]. Laboratory studies of these processes under conditions appropriate for the diffuse interstellar medium remain to be performed.

3. Interstellar molecular clouds

(a) The interclump medium

Molecular clouds are clumpy, with densities ranging from a few thousand H$_2$ cm$^{-3}$ extending over large regions, to number densities at least 1000 times larger in small compact cores. We discuss first the relatively low-density background gas ($n_{H_1}$ approx. $3 \times 10^3$ cm$^{-3}$, $T_K$ approx. 30 K), in which typical path lengths have optical depths in the visual of approximately 3–10. Thus, starlight (especially the more heavily extinguished UV starlight) is largely excluded from these regions. This interclump gas was detected first in (1–0) rotational emission from gaseous CO at 2.6 mm. The hydrogen is largely in H$_2$, most of the available gaseous carbon is in CO, and the residual gaseous oxygen is largely atomic.

The importance of the gas–dust interaction in these regions is demonstrated clearly in the detection of ice formation on dust surfaces where the optical depth in the visual is larger than a critical value, typically around 3 for molecular clouds in the constellation of Taurus, but the value varies from region to region. The ice is detected by absorption near 3 $\mu$m (against a background source such as a bright star), associated with the O–H stretching mode in H$_2$O ice. Other species also detected by stretching mode vibrations (rotational modes are suppressed in these spectra) are CO, CO$_2$, CH$_3$OH, H$_2$CO, NH$_3$ and some other species; H$_2$O is the dominant constituent of all detected ices.

Ice features are very weak or non-detected below the critical optical depth, and the strength of the H$_2$O and CO absorptions rises with optical depth. Although the ices are now well studied on many lines of sight, the reason for the onset of the ices at some critical value of optical depth remains obscure. It is clear, however, that there is a difference between H$_2$O and CO ice species: because H$_2$O is normally a very minor constituent of the interstellar medium, the H$_2$O molecules must be made in situ, and a high proportion of them must be retained to form the ice, whereas CO molecules—abundant in molecular clouds—are simply adsorbed from the gas phase on to the surface and incorporated into the ice. This causes some chemical layering in the ice, with modification of the spectra of adsorbed species, depending on the nature of its environment [32].

Various reasons have been suggested for the onset of the ices above a critical optical depth. The suppression of photodesorption at sufficient depths seems initially plausible, but a consideration of the ice onset on different lines of sight argues against this [33]. It is possible that a change in the chemical nature of the carbonaceous dust surface from sp$^2$ to sp$^3$ may affect the
binding of adsorbed H2O molecules. It is also likely that the gas density plays a role; if the flux of gaseous O atoms is sufficiently high, then perhaps a monolayer coverage can be established so that any desorption mechanisms capable of removing the more weakly bound ‘lone’ H2O molecules are saturated by the higher flux of O atoms.

The chemical composition of the ices varies from one line of sight to another, suggesting that the ice chemistry is influenced by local conditions. However, the solid-state chemistry does not reflect the local gaseous chemistry. A good example of this is CO2, which is very rare in the gas phase under cold conditions, whereas it may be the second or third most abundant molecule in the ices (typically approx. 20% relative to H2O). It is now accepted that CO2 is derived from CO in the ice through some solid-state chemical processing, probably initiated by cosmic rays or cosmic-ray-generated UV. One possible route involves the dissociation of water by cosmic rays and the subsequent fast reaction of CO with OH to form CO2 [34]. Similarly, the abundance of methanol in ices is typically a few per cent relative to H2O in the ice. This is a much higher proportion than can be accounted for by the freeze out of CH3OH molecules formed in gas-phase reactions. It is now accepted, and is supported by several computations and laboratory experiments [17,18,35,36], that the high abundances of methanol and formaldehyde detected in interstellar ices are a consequence of successive hydrogenation of CO molecules within the ice, for example,

\[
\text{CO} \rightarrow \text{HCO} \rightarrow \text{H2CO} \rightarrow \text{CH3O} \rightarrow \text{CH3OH},
\]

in low-temperature (approx. 10 K) reactions with H atoms released by cosmic-ray or UV interaction with the H2O ice.

(b) Dense cores in clouds: pre-stellar

Observations of molecular clouds in rotational emission lines of species such as HCO+, N2H+ and CS reveal the presence of dense cores against the background of less-dense gas. These cores are cold (T_K approx. 10 K), and typically about 100 times denser than the background gas, making the core number density of the order of 10^5 cm^{-3}. The optical depth in the visual through these cores is about 10 (or about 30 in the UV). These tracer molecules, and many others, are formed in gas-phase cosmic-ray-driven chemistry. Emissions by molecules such as CO isotopologues, OH and H2O are effective coolants for the cores, so that gravitational collapse may occur in cores that are sufficiently massive to be gravitationally unstable. If so, these objects represent the earliest stages of star formation; this is an important reason to study them. Gravitationally stable cores also exist and are exceptionally quiescent. They may provide a good example of steady-state interstellar chemistry, in which freeze out of species on to dust grains is balanced by desorption processes discussed later in this section.

As the density increases from the background gas to that of the cores, the frequency of collisions between dust grains and gas-phase species increases and eventually becomes dominant. Ices accumulate on the grains and are detected through pure vibrational spectra of species in the ice. Initially, the ice is mainly water, carbon monoxide and possibly ammonia, but solid-state chemical processing, driven by the passage of cosmic rays or by the cosmic-ray-induced UV radiation field to add carbon dioxide, methanol and formaldehyde to this list, during the relatively low-density period when cores begin to form from the background gas. This latter radiation field is distinct from the interstellar radiation field of starlight, which does not penetrate the cores. It is created in the recombination of hydrogen molecular ions that have been ionized by cosmic-ray impact on H2. We show in table 1 observational results for the composition of ices along two different lines of sight: towards a high-mass star and towards a low-mass star.

The processing of ices by particle or UV fields has been a fertile area for study in the laboratory [41,42], and many of the laboratory results have been incorporated in models of solid-state chemistry in ices [43,44]. The models have many unknown parameters, including mobility of reactive species within the ices and of the energy budget in the solid-state reactions. Nevertheless, the model results compare well with observational data.
Table 1. Column densities (cm$^{-2}$) of ices towards a low-mass source (derived from [32,37]; second column) and a high-mass source (derived from [38–40]; third column).

<table>
<thead>
<tr>
<th>ice</th>
<th>IRAS 08242–5050</th>
<th>W33A</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>$7.8 \times 10^{18}$</td>
<td>$1.3 \times 10^{19}$</td>
</tr>
<tr>
<td>HCOOH</td>
<td>$2.1 \times 10^{17}$</td>
<td>$6.5 \times 10^{17}$</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>$3.9 \times 10^{17}$</td>
<td>$1.9 \times 10^{18}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>$3.9 \times 10^{17}$</td>
<td>$7.8 \times 10^{16}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$2.2 \times 10^{18}$</td>
<td>$1.4 \times 10^{18}$</td>
</tr>
</tbody>
</table>

Because the temperatures in molecular clouds and pre-stellar cores are always low, approximately 10 K, thermal desorption is negligible. However, non-thermal processes may drive intermittent desorption. The cosmic-ray-induced radiation field is a UV field capable of photodesorbing H$_2$O and other species from mixed ices. Direct passage of cosmic rays through dust grains deposits some heat along the penetration path through a dust grain, and this may cause evaporation at the entry and exit points [45]. Reactions of atomic hydrogen on the surface to form H$_2$ also deposit heat into the grains, as shown by the London experiments [23]. This may also drive a desorption of weakly bound species near the reaction site [46]. Finally, if the population of radicals (including atomic H) can build up to a critical level in and on the grain, then runaway explosions may return material to the gas [47,48]. Three-body reactions in the expanding (yet initially very high density) gas may lead to rapid formation of signature species [49].

(c) Dense cores in clouds: post-stellar

In regions of massive star formation, there are found very dense ($n_H$ approx. $10^7$ cm$^{-3}$), warm ($T_K$ approx. 200 K) and tiny-scale (approx. 0.01 pc) objects that have extremely high optical depth in the visual (approx. $10^3$). These objects are called ‘hot cores’ and they are found to exhibit a very rich gas-phase chemistry, including some large molecular species (relative to those found in lower density regions) such as ethanol, methyl formate, methyl cyanide, etc. Such molecules are regarded as signatures of hot cores.

These hot cores are considered to be the result of the gravitational collapse of lower density pre-stellar cores that are gravitationally unstable; the collapse continues until star formation begins. At that point, the protostar is a powerful source of infrared radiation that heats the dense core from its originally low temperature (approx. 10 K) to the temperatures observed in hot cores, and begins to arrest the collapse.

Although detected in the gas phase, these complex molecular species are believed to be the result of solid-state chemistry continuing during the collapse, as described in the previous section. The molecules are detected in the gas phase because the warming of the grains by infrared radiation from the embedded protostar leads to desorption of the ices. Early modelling of the desorption process assumed that it was abrupt, and that all the material of the ices was instantaneously transferred into the gas phase at some critical temperature. In fact, the warming process is likely to be slow and to resemble laboratory studies of temperature-programmed desorption (TPD), though with heating rates much slower than in the laboratory.

Collings et al. [50] have studied TPD for mixed ices of compositions appropriate for the interstellar medium. They have shown that desorption from these mixed ices occurs in several distinct and very narrow temperature bands. In the lowest temperature band, desorption occurs from pure CO (or other weakly bonded material). In the next highest temperature band, desorption occurs from monomolecular layers on more refractory surfaces. As the temperature rises until the next temperature band is reached, amorphous H$_2$O ice crystallizes, and desorption of interstitial species may occur in the so-called volcano event. Finally, when H$_2$O ice itself desorbs, all remaining species in the ice are ‘co-desorbed’.
Although these TPD experiments were carried out in conditions far from those pertaining in hot cores, it is possible to convert the positions of the laboratory-measured temperature bands to values appropriate to the astronomical conditions of a very slow warming rate. These revised temperature bands were computed, and we have explored the consequences for hot core chemistry [51]. We found that the values of the temperatures of the desorption bands for hot cores depend on the heating rate, and consequently on the mass of the protostar. For a 10 solar mass protostar, the volcano and co-desorption events occur at 88 and 99 K, whereas for a 25 solar mass protostar (which evolves more rapidly), these bands shift slightly to 90 and 106 K.

Models of hot core chemistry based on this laboratory work give results that are strikingly different from those that assume instantaneous desorption of all the ice. There is strong time dependence in the predicted chemistry because different species are injected into the gas phase at different times. In particular, the species H$_2$S, SO, SO$_2$, OCS, H$_2$CS, CS, NS, CH$_3$OH, HCOOCH$_3$, CH$_2$CO and C$_2$H$_5$OH all show a strong time dependence [51]; this may be a useful signature of the time evolution of the warm-up phase as the protostar moves towards the main sequence.

The formation of lower mass stars follows a similar process, and regions forming low-mass stars contain objects similar to hot cores, here termed ‘warm cores’ (some authors use the name ‘hot corino’). The temperatures of warm cores are lower than those of hot cores because the less-massive protostar is much cooler and it evolves more slowly, so the heating rate is smaller. The warm cores are, in general, small compared with hot cores; however, their chemistry is largely similar. A well-studied warm core, IRAS 16392-2422, contains a solar mass star. It exhibits spatially abrupt drops in abundance in species such as H$_2$O, SiO and H$_2$CO with increasing radius from the protostar. We have a model [52] of such an object that describes the chemistry of a warm core, up to species as large as ethanol and methyl formate; this model shows that the abrupt changes correspond to the desorption bands found in the TPD experiments of Collings et al.

Thus, reliable TPD data allow a significant improvement in our understanding of the initial stages of star formation.

4. Chemistry in galaxies beyond the Milky Way

Molecules were first detected in nearby external galaxies in the 1970s [53]. Subsequently, the remarkable detection of CO emission in a gravitationally lensed quasar at a red-shift of 6.4 [54] showed that chemistry was occurring in the Universe from very early times and is therefore widespread at the present epoch. Because nearly all galaxies show signs of optical extinction and many are strong infrared emitters, it is clear that dust grains are also present in external galaxies. Hence, the gas–dust interaction that enables surface chemistry to play a role in the Milky Way may also occur in external galaxies.

(a) Galaxies

Unfortunately, our knowledge of the nature of extragalactic dust is rather poor, and so it is often assumed that the dust is similar in composition and grain size distribution (and therefore in optical and chemical properties) to that of the Milky Way. However, it seems likely that the mass of material in dust is determined in part by the availability of elements other than hydrogen and helium (called the ‘metallicity’ by astronomers). The metallicity in external galaxies can be measured from atomic emission lines in stars and nebulae; it ranges from slightly above the Milky Way value to values that are typically a factor of 10 smaller. Typically, the metallicity of high redshift galaxies—and therefore the dust:gas ratio—may be an order of magnitude less than in the Milky Way. As mentioned below, this may be an optimistic assumption.

Interstellar ices outside the Milky Way have only been observed so far towards young stellar objects in the Large Magellanic Cloud [55] and in few ultra luminous infrared galaxies [56]. However, it seems likely that surface processes are important because all the detected
extragalactic gas-phase species form through a gas-phase reaction network that requires the presence of abundant H$_2$, efficiently formed on dust (see §2a). Assuming this to be so, we may consider if there are significant differences between surface chemistry in the Milky Way and in external galaxies, beyond those already mentioned (fairly minor changes in metallicity with proportional changes in the gas:dust ratio and in the H$_2$ formation rate; and as yet unknown changes in the physical and chemical properties of dust grains).

The main differences are likely to arise in the most energetic galaxies, i.e. starbursts initiated in galaxy collisions, and galaxies with active nuclei that are powered by the accretion of material on to a massive black hole. In these types of galaxy, the two main energy sources of astrochemistry—fluxes of cosmic rays and of electromagnetic radiation—are likely to be much more intense, possibly by factors of approximately $10^4$, than those in the Milky Way. Both types of galaxy should have more violent magnetohydrodynamics than in the Milky Way. There are various likely consequences for surface science in these galaxies.

First, the processes destroying dust grains—grain–grain collisions and hot gas sputtering—are enhanced, so that grain populations may be reduced (beyond the factor related to metallicity, as described earlier), and the remaining grains driven to smaller sizes. Because grains are observed to be present in external galaxies, we infer that their optical properties (at least, in starburst and active galaxies) are different and their ability to shield cloud interiors from external radiation fields is diminished. The capability of surface processes to contribute to chemistry in such galaxies to the extent that they do in the Milky Way is therefore unclear; smaller grains may be more chemically active. Chemistry (gas phase and solid state) in galaxies where dust extinction is caused only by small grains needs to be explored.

Second, the surface and bulk of the grains will be more defected by high-energy cosmic rays than in the Milky Way, creating many more chemically active sites per unit area of surface. Grains in active galaxies may therefore be more effective catalysts than those in the Milky Way, partially offsetting the reduction in grain numbers per unit volume. Experiments exploring the chemical activity of carbon and silicate surfaces under increasing particle fluxes would be useful.

Third, grain temperatures are likely to be higher than in the Milky Way where, in molecular clouds, temperatures of approximately 10 K are measured. Both cosmic rays and far-UV radiation are important heating sources for dust grains. If their fluxes are increased by factors of approximately $10^4$, then a crude estimate suggests that grain temperatures would increase by a factor of about seven compared with Milky Way grains (assuming that smaller grains which may exist in such galaxies are unchanged in their cooling ability). At temperatures around 70 K, freeze out of many species would be inhibited and the desorption of molecules from ices would be enhanced. It is unclear whether ices would form and if so whether the composition would be like those of the Milky Way. On the basis of this estimated temperature, CO could not be retained in the ice for very long, and its chemical derivatives (H$_2$CO, CH$_3$OH, CO$_2$, HCOOH, HCOOCH$_3$, etc.) would not be formed in as large quantities as in Milky Way hot cores. This argument predicts that hot core molecules may be different, or have different relative abundances in starbursts and active galaxies. The detection of gaseous HNCO and CH$_3$OH in a starburst galaxy, NGC 253 [57,58], suggests either that normally rather slow gas-phase routes for these species are improved in this galaxy, or that ices do exist in spite of the elevated temperatures, and that chemical processing does occur. Experiments exploring solid-state chemistry in ices of varying composition and temperatures would be useful.

Fourth, the high photon arrival rate in starburst and active galaxies is comparable to or larger than the H-atom arrival rate at surfaces, reversing the situation typical in the Milky Way. It is unclear what effect this may have on the H$_2$ formation rate. It is possible that photodesorption of H atoms at active sites may be faster than previously considered for the Milky Way, so that H$_2$ formation is suppressed compared with the Milky Way. Experiments exploring high radiation intensity regimes would be useful.
Table 2. Summary of surface processes active in the different regions of the interstellar medium.

<table>
<thead>
<tr>
<th>region</th>
<th>surface and solid-state processes</th>
<th>state of current data</th>
<th>recommended work</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffuse clouds</td>
<td>H₂ formation</td>
<td>good</td>
<td>further work on energy budget</td>
</tr>
<tr>
<td></td>
<td>hydride formation</td>
<td>nil</td>
<td>hydrogenation of O, N, C⁺, S⁺</td>
</tr>
<tr>
<td>molecular clouds</td>
<td>ice mantle onset</td>
<td>poor</td>
<td>H₂O desorption, dependence on O-atom flux, and on nature of surface</td>
</tr>
<tr>
<td></td>
<td>ice mantle composition</td>
<td>good</td>
<td>nil</td>
</tr>
<tr>
<td>pre-stellar cores</td>
<td>ice processing</td>
<td>fair</td>
<td>photodissociation by UV, photoionization by cosmic rays, radical mobilities, molecular desorption energies</td>
</tr>
<tr>
<td>post-stellar cores</td>
<td>desorption</td>
<td>fair</td>
<td>TPD of mixed ices; chemistry in the evaporate</td>
</tr>
<tr>
<td>active galaxies</td>
<td>exposure to very high fluxes of UV and cosmic rays</td>
<td>nil</td>
<td>do ices survive? nature of chemical processing</td>
</tr>
<tr>
<td>galaxy clusters</td>
<td>additional heating, higher</td>
<td>nil</td>
<td>ice processing and desorption at high temperatures</td>
</tr>
<tr>
<td></td>
<td>temperatures</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) Galaxy clusters

NGC 1275 is a galaxy at the centre of a cluster of about 1000 galaxies. There are strong interactions between the galaxies in the cluster, involving infall of material on to NGC 1275 and outflowing material from it. Turbulent interfaces are believed to be responsible for creating huge filaments of gas and dust extending out from NGC 1275 [59]. These are typically 100 pc thick and some tens of Mpc long. Therefore, they probably contain enormous amounts of matter, comparable to a galactic mass. The filaments are observed to radiate in atomic lines in the optical, in H₂ infrared ro-vibrational lines, and in millimetre rotational lines of CO [60–62]. A current concern is that a very high heating rate is required to maintain these observed emissions. This heating may arise from dissipation in the turbulent interface or from high cosmic-ray rates.

From the perspective of surface science, we can ask whether surface and solid-state chemistries occur on any dust grains that may be present in these filaments. Our models [63] and observations [64] suggest that high-dissipation heating rates are not required, and that heating by cosmic rays at rates 100 or more times the Milky Way rates should suffice to provide the observed excitation. We estimate from this that the grain temperature may be raised to about 40 K. This elevated grain temperature puts in jeopardy the retention of CO in ices, although H₂O ice should survive. Hence, this appears to be a situation in which surface chemistry can occur, but in a different form from that in the Milky Way.

5. Conclusion

Table 2 summarizes the conclusions in this paper and lists problems where further laboratory or theoretical work would greatly enlighten studies of surface and solid-state astrochemistry. The chemical properties of dust grains in external galaxies may account for the greatest uncertainty in the table.
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