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Chemistry on Interstellar Grains

E Herbst¹, Q Chang², H M Cuppen²

¹ Departments of Physics, Astronomy, and Chemistry, The Ohio State University, Columbus, OH 43210, USA

² Department of Physics, The Ohio State University, Columbus, OH 43210, USA

E-mail: herbst@mps.ohio-state.edu

Abstract. In this review, our current knowledge of the chemistry that occurs on cold interstellar grain surfaces is examined. The formation of molecular hydrogen from hydrogen atoms is emphasized. Various methods of modeling diffusive reactions on grain surfaces are illustrated, including the rate equation method, and two basic stochastic approaches. The results of a detailed Monte Carlo method - the continuous-time random-walk approximation - in which the problem of random walk in two dimensions is treated exactly, are shown and analyzed for the case of H₂ formation. Both homogeneous surfaces such as olivine and amorphous carbon and inhomogeneous surfaces are studied. Results from this method show that (a) inhomogeneous surfaces allow efficient H₂ formation over wider temperature ranges than do homogeneous surfaces, and (b) the reaction efficiency declines for grains smaller than a certain size, but the effect is smaller for inhomogeneous surfaces.

1. The ISM and interstellar grains

The interstellar medium (ISM) in our Milky Way Galaxy and others is a rather complex affair. There is much low density material, both in neutral and ionized form. The colder and denser material is condensed into mainly neutral objects known as clouds, which contain both gas-phase atoms and molecules and tiny particles, known as dust or as interstellar grains [1]. Both the gas and particulate phases derive from matter that is ejected from old stars, either explosively, as occurs in the case of supernovae, or more gently, as occurs in the case of low-mass stars, which possess extended atmospheres, or envelopes, once they live past their main-sequence (hydrogen-burning) stages. Clouds have a wide range of gas densities, and the terms “diffuse” and “dense” are often used to distinguish those of lower and higher densities, respectively. Sometimes, the term “translucent” is used to describe material of intermediate density. Very large clouds are comprised of gaseous and dusty material of significantly different densities. Typical elemental abundances for the gas-phase of diffuse and dense regions, as well as the so-called “cosmic abundances” appropriate for stellar atmospheres (mainly main-sequence stars), are shown in Table 1 [2, 3, 4]. The numbers are normalized with respect to the most abundant element, hydrogen. The abundances of the heavier elements in the gas-phase of interstellar clouds are lower than in stellar atmospheres because some of the elements are likely to be found partially in the dust particles. The stronger depletion of the heavier elements from the gas phase of dense clouds, as seen in Table 1, suggests that a greater portion of the material is solid-state in nature.

Diffuse regions have gas densities in the range 10^2 - 10^3 cm⁻³, gas-phase temperatures of 50-100 K, and grain surface temperatures of perhaps 20 K [5]. Ultra-violet and visible radiation from stars tends to penetrate through diffuse material, and photodissociation and photoionization

processes are important in reducing the concentrations of molecules [6]. Indeed, the gas consists mainly of atomic material except for the case of hydrogen, the dominant element, which is equally divided into neutral atoms and molecules. Small abundances of other diatomic molecules (e.g. CH, CH⁺, OH, NH, C₂, CO) and two triatomic species (H₃⁺, C₃) have been detected in infra-red, optical and ultra-violet absorption using background stars as lamps [6]. Along lines of sight to distant radio continua, certain other polyatomic species can be detected in absorption via their rotational spectra [7]. Diffuse material can exist by itself, along the line of sight to stellar or non-stellar lamps, or it can exist in giant clouds along with denser material. The dust in diffuse regions appears to be a mixture of amorphous silicates and carbonaceous material, either as separate grains or combined into more complex structures [1, 5, 8, 9]. Although astronomers used to think of a “standard” size of 0.1 μm for grains, it is now known that there is a distribution of sizes, with a dependence on the radius r raised to the power -3.5; i.e., there are many more smaller grains than larger ones [9]. Indeed, some astronomers now refer to different classes of grains depending on size: there are standard grains, very small grains, and, at the smallest sizes, PAH-like species composed of aromatic matter but possibly less hydrogenic in nature than laboratory PAH’s [5, 8, 10]. A standard estimate for the abundance of PAH species with respect to hydrogen is $10^{-6} - 10^{-7}$ so that much of the element carbon exists in this form. Some typical ranges of grain radii are: 0.03 - 3 μm for standard grains, 2-10 nm for very small grains, and 0.5 - 1.0 nm (5 - 10 Å) for PAH’s. Of course, grains are not spherical and should not be labeled by radius; it is more likely that grains have some fluffy form [11].

Table 1. Elemental abundances with respect to total hydrogen.

Element	Cosmic	Diffuse Gas	“Low-Metal” (Dense Gas)
C	4.0(-04)	1.32(-04)	7.3(-05)
O	7.4(-04)	3.2(-04)	1.76(-04)
N	9.3(-05)	7.5(-05)	2.14(-05)
S	2.6(-05)	1.86(-05)	8.0(-08)
Si	3.5(-05)	2.9(-05)	8.0(-09)

Dense clouds, often detected as cores within giant molecular clouds, are associated with high enough concentrations of gas ($10^4 - 10^6 \text{ cm}^{-3}$) and dust that the so-called “extinction” is very high, and little if any visible and ultraviolet light gets through them. Most of the extinction is continuum extinction caused by the dust particles, which both scatter and absorb radiation with an efficiency that increases with decreasing wave length, as in Mie theory [8]. The percentage of the material in dust particles is estimated to be about 1% by mass, a figure similar to that in diffuse clouds. The temperature can be as low as 10 K, and this value pertains to both gas and dust. Virtually all of the element hydrogen has now been converted into molecular form, although a small but detectable amount of atomic hydrogen remains [12]. Rich rotational spectra, detected typically in emission due to collisional excitation, show the gas to be overwhelmingly molecular, with species up to more than 10 atoms in size (see, e.g., the website <http://astrochemistry.net/>). It is actually difficult to determine the elemental abundances in the gas phase, and the values shown in Table 1 are a well-known set of estimates known as “low metal” abundances [4]. Some molecular fractional abundances (concentrations with respect to molecular hydrogen) for the well-studied dense cloud core TMC-1 are shown in Table 2 [13]. It can be seen that only CO takes up a significant percentage of the elemental abundances of its constituent atoms. From infrared absorption spectra of the grains, we learn that in addition

to cores of silicates and carbon, icy mantles exist containing mainly water ice, but also carbon dioxide and carbon monoxide ices, plus smaller amounts of methanol and possibly more exotic species [3]. The mantles arise from a combination of chemistry occurring on the grain surfaces and accretion of molecules from the gas. Mantles of up to 100 monolayers are observed, and the size distribution of these core-mantle particles is highly uncertain. The amount of water ice on grain mantles is comparable to the amount of gaseous CO.

In certain dense cores associated with star formation, accretion onto grains becomes an even more salient feature. In cold pre-stellar cores, for example, where the initial collapse of a dense core to form a low-mass star has started and is still isothermal in nature, the very dense centers appear to be very strongly depleted of most species in the gas with the exception of hydrogen and helium [14, 15, 16]. Pre-stellar cores are just an initial stage in the evolution of cold cores into low-mass stars. Later stages, in which the collapse becomes adiabatic and the center heats up, are known as “protostellar.” In the general vicinity of protostars, there are regions in which mantles appear to evaporate from dust particles as the temperature rises, changing the chemical characteristics of the gas-phase from a mainly unsaturated (hydrogen-poor) to a saturated (hydrogen-rich) chemistry [17, 18]. The strongest evidence for such changes occurs in so-called hot molecular cores with temperatures of 100 - 300 K, found in the vicinity of high-mass star formation, where high abundances of organic species such as ethanol, methyl formate, and dimethyl ether are detected [19]. Three of the best-known hot cores are the “Hot Core” and “Compact Ridge,” in the Orion giant molecular cloud, and the “Large Molecule Heimat,” seen in the giant Sagittarius B2 cloud, near the center of our galaxy [19, 20, 21].

In the case of low-mass star formation, the newly-formed star is often seen with a disk of dense gas and dust rotating around it, known as a “protoplanetary disk.” These disks are quite heterogeneous in density and temperature, depending on how far the material is from the newly-born star. Material in the so-called ‘midplane’ that is dense and far enough away to remain cold [22, 23] is, as in pre-stellar cores, also virtually bereft of gas-phase material heavier than hydrogen and helium. As protoplanetary disks age, swollen dust particles eventually coagulate to form larger structures. The term “debris disk” is used for an evolved disk in which individual dust particles are seen to disappear, presumably to form planets.

Table 2. Some observed fractional abundances (with respect to H_2) in TMC-1.

Species	Abundance	Species	Abundance
CO	8(-5)	OH	2(-7)
C_4H	9(-8)	HCN	2(-8)
HNC	2(-8)	NH_3	2(-8)
HCCCN	2(-8)	cyclic- C_3H_2	1(-8)
HCO^+	8(-9)	HCNH^+	2(-9)
HCS^+	4(-9)	HCCCNH^+	1(-10)

2. Surface Chemistry at Low Temperatures

Although most of the molecules detected in the gas-phase of interstellar clouds appear to be formed via sequences of gas-phase reactions [13, 24, 25, 26], this is not true for all species in all types of sources. The most important exception remains the formation of molecular hydrogen from precursor hydrogen atoms, a process that must be very efficient to form copious amounts

of H_2 even in diffuse clouds. The most simple gas-phase alternative, the reaction



cannot occur efficiently because the only mechanism to stabilize the product at low densities is the emission of radiation, a very unlikely process for a variety of reasons [27]. At higher temperatures, as occur for example in the early universe [28], the two-step process,



occurs efficiently, but in the cold interstellar medium, the only process capable of converting atomic to molecular gas occurs on the surfaces of dust particles. This process has been invoked by astronomers for many years now [27], but it is only recently that laboratory evidence has confirmed that the reaction occurs on surfaces resembling those of interstellar particles [29, 30, 31, 32, 33]. Although the actual mechanism for the reaction is still in some dispute, the most probable one is the so-called Langmuir-Hinshelwood mechanism, in which the two hydrogen atoms land on a grain, stick with high efficiency, diffuse rapidly over the surface, find one another, and form a temporary chemical bond that is stabilized by the loss of energy to the phonon modes of the grain. Moreover, it is likely, and may even have been witnessed in recent experiments, that at least some of the nascent hydrogen molecules are immediately ejected from the surface. For such a mechanism to occur at low temperatures, at least one hydrogen atom must be very weakly bound to the surface, a binding known as “physisorption.” Strong binding, known as “chemisorption”, does not lead to diffusive motion at low temperatures. Chemisorption does not occur at low temperatures for many systems because there is often an activation energy barrier to the formation of the surface-atom bond caused by the reconstruction of the surface [34, 35]. If chemisorption does occur, a mechanism for reaction is the so-called “Eley-Rideal” process, in which a gas-phase hydrogen atom attacks a chemisorbed atom on the grain surface. A similar and only partially distinct mechanism is known as the ‘hot atom’ process; here the gas-phase atom lands near the stationary surface atom, and is able to move to it along the surface before being thermalized [34].

The formation of molecular hydrogen is clearly not the only example of surface chemistry that can occur in interstellar clouds. Astrochemists have focussed on atomic hydrogen as the most important reactant in other processes, since, until totally converted to its molecular form, it is abundant, its low mass allows it to diffuse quickly over a surface if it is only physisorbed, and it is reactive. In addition to reacting with itself, hydrogen atoms are thought to react with slower-moving heavier species that stick to dust grains [36]. Most of the reactions are, as is the formation of H_2 , association reactions, in which one product is formed and stabilized by a third body; namely, the grain. Among the most important processes are those that convert atomic oxygen into water ice:



which are thought to be the main production route leading to the large abundance of water ice in dense cold sources. Similar mechanisms convert atomic nitrogen into ammonia, and atomic carbon into methane. There is even evidence (see below) that carbon monoxide, formed in the gas, can be hydrogenated into formaldehyde (H_2CO) and even methanol (CH_3OH) although there is also some chemical activation energy involved in the process [37]. Besides reactions involving hydrogen atoms, there are other association reactions thought to be critical, such as that leading to the spin-forbidden production of CO_2 :



for which there is only ambiguous laboratory evidence [38].

Even with the results of recent experiments, surface chemistry is generally far more poorly understood than gas-phase chemistry, and in the case of interstellar dust grains, there are additional problems given our lack of a detailed knowledge of the physical nature of the surface. Among the problems faced by astrochemists are: (i) the detailed mechanism for the formation of molecules (Langmuir-Hinshelwood vs Eley-Rideal); (ii) the dependence of the rate of surface reaction on grain size, the possible existence of a grain mantle, the probable fluffy nature of interstellar grains, the smoothness or roughness of the surface, and unknown energy parameters, (iii) whether or not the rate equations used by surface chemists even apply to chemistry on small grain particles, and (iv) how products can desorb from grain surfaces back into the gas. With regard to the last problem, it is clear from observational evidence that unless a star forms nearby and the temperature rises, most heavy molecules formed on grains remain there to constitute the mantles. Nevertheless, there are inefficient non-thermal desorption mechanisms that probably return some material to the gas, albeit with uncertain efficiencies [39, 40].

A final problem concerns the likely charge on interstellar grains. Because in a thermal medium, electrons travel more rapidly than heavy positive atomic and molecular ions, it is likely that the grains are negatively charged unless photoelectric effects dominate [41, 42, 43]. In the simplest view, the presence of excess negative charge is likely to repel other electrons from attaching themselves to the grains. Positive ions, on the other hand, will probably be neutralized upon sticking to grains unless the negative charge is truly localized. Since the neutralization energy is large, it is likely that the neutral product will be desorbed from the grain surface and it is possible that it will also dissociate in the process [44]. The net result is that we needn't worry about the existence of positive ions on grain surfaces.

3. Recent Surface Experiments

In recent years, a number of useful experiments have been undertaken on the surface formation of molecular hydrogen and other species at low temperatures on realistic analogs of interstellar grains [29, 30, 31, 32, 33, 38, 45]. All experiments have been performed on cold surfaces rather than small particles. The experiments on H_2 formation have been of two types: (a) those designed to determine the internal and translational energy of the product as it leaves the surface and (b) those designed to measure and understand the rate and mechanism of the reaction. Results for H_2 formation on ice [45] and graphite [46] show that much of the exothermicity of reaction (4.5 eV) winds up in the grain rather than in either the internal modes of the H_2 molecule or the translational energy between the molecule and the surface. The experiments of the second type are of more concern here. These are most often accomplished by the technique of *temperature programmed desorption*, or TPD for short [34], in which the H atoms are deposited with as small a deposition rate as possible on a very cold surface, and the temperature is subsequently raised slowly, leading to both diffusive reaction and desorption. TPD experiments of this type were done by a group headed by Vidali and Pirronello on olivine (a poly-crystalline metallic silicate), amorphous carbon, and two types of amorphous water ice [29, 30, 31, 32]. To improve the signal-to-noise, the studies on the first two surfaces were accomplished for HD formation, while on water ice, the experiments studied the formation of H_2 , D_2 , and HD. In the simplest analysis, the data can be analyzed to yield single values for the barrier against diffusion on the surface and the energy needed to desorb both reactant and product. Such an analysis of the experiments on olivine and amorphous carbon [47] showed that diffusion of H and D atoms occurs by thermal activation (hopping over barriers) rather than quantum mechanical tunneling and that single energies, typical of physisorption, are all that is needed to describe diffusive barriers and desorption. No distinction was made between hydrogen and deuterium atoms. In addition, it was found that a certain percentage, perhaps half, of the newly formed H_2 species are ejected immediately rather than thermally evaporating afterwards. The analysis of

the reaction on (and within) water ice is more complex; for example, three different sites must be assumed for the molecular hydrogen product [48].

Challenges to both the analysis and experimental details of the work of the Vidali et al. group have been made. The challenge to the analysis of Katz et al. [47] is based on its simplicity; Cazaux & Tielens [49] have performed an analysis with additional variables in which H and D are treated distinctly and in which both chemisorption and physisorption binding sites are allowed. The argument in favor of chemisorption comes from theory and experiments on graphite at high temperature [35, 79] although according to theory these sites cannot be accessed without overcoming a barrier of 0.2 eV, which would be much too high for cold atoms in space. The approach of Cazaux & Tielens [49] obviates this problem by postulating that H atoms in sites with physisorption can transfer horizontally to sites with chemisorption without such a large barrier. The technical term for such a process in surface science is “precursor mediated adsorption [34].” Whether or not such a process occurs for typical interstellar grains at low temperatures is of course not known. Additional TPD experiments on realistic grain analogs over wide ranges of temperatures are needed since such experiments will yield more information on possible sites of chemisorption and how easy it is to access them.

There is also some disagreement about the experimental TPD results, at least for ice. A group in Denmark [33] has studied the formation of H_2 on what they term “amorphous solid water” (ASW) and found that H_2 is formed immediately at the temperature of deposition, possibly by tunneling under diffusive barriers. The evaporation as a result of subsequent heating up is analyzed not in terms of the diffusive formation of H_2 but in terms of the evaporation of already-formed H_2 from sites of differing binding energy, since ASW is a rather complex surface with a distribution of binding energies. Whether the group of Vidali et al. or of Hornakaer et al. is correct is not yet known to outsiders such as ourselves. It is of course possible that both groups are correct: the flux of H atoms in the Danish experiment is higher than in the Vidali et al. experiments and the greater proximity of H atoms to one another may well allow more efficient reaction at lower temperatures. More work clearly remains to be accomplished.

Besides the experimental work on H_2 formation, work has been done on the low-temperature surface formation of CO_2 from CO and O [38], on the hydrogenation of atoms such as N into ammonia [51, 52], and even on the hydrogenation of CO into formaldehyde and methanol [37], although there is still some disagreement about some of the results. The experiments have been done mainly on water ice, via thermal desorption and infra-red spectroscopy. The surface is a reasonable choice for dense cold clouds. From the rate of production, chemical activation energies can be determined, although the values obtained are dependent on the choice of rate law (see below) and whether or not the reaction proceeds via transmission over a barrier or tunneling under it [53].

If we consider the totality of surface experiments done to date, we can generalize that laboratory work is at the stage where it has confirmed the view of astrochemists as to what types of diffusive thermal processes can occur on low temperature surfaces, but is only approaching the stage where it can give us unambiguous parameters to be used to determine actual rates under interstellar conditions.

The experiments discussed above pertain only to *thermal* reactive processes. In addition to such reactive processes on grains, there is also the possibility that energetic particles (e.g. hard photons, cosmic rays) can drive a photochemistry leading to the production of rather complex species on grain surfaces. Many experiments have been performed in the laboratory to study these processes, but typically at fluxes far greater than are relevant to the interstellar medium [54, 55, 56, 57]. Since detailed modelling including such processes is rarely attempted, we will not discuss the topic in this review further except to issue a call for investigators to attempt to model the photochemistry.

4. Modeling Diffusive Surface Chemistry

Given what is known about surface reactions, especially the diffusive, or Langmuir-Hinshelwood, mechanism, how do we go about modeling the rates of important surface reactions on interstellar particles? It is useful to think of the surfaces of these particles as lattices with specific numbers of lattice sites, where adsorbates such as atomic hydrogen can bind. For spherical grains, the relationship between the number of lattice sites N and the diameter r of the grain is given by the equation:

$$N = 4\pi r^2 s, \quad (7)$$

where s is the surface density of lattice sites [34]. The experimentally derived surface site density for olivine is $2 \times 10^{14} \text{ cm}^{-2}$ [47] so that our olivine grains with a ‘standard’ radius of $0.1 \text{ } \mu\text{m}$ have $N \approx 10^5$. To determine the rates of diffusive processes, we must consider how adsorbates such as H travel from site to site and what they do when they find one another. We will consider both the rate-equation approach [36, 58] and several, more advanced, stochastic methods [59, 60, 61, 62, 63].

4.1. Rate Equations

Consider two species A and B that are to react on a surface via the Langmuir-Hinshelwood mechanism without activation energy. Let us initially assume B to be stationary and follow one A species. The rate of hopping k_{hop}^A (s^{-1}) from the site where A resides to a nearest neighbor site is given by the equation

$$k_{hop} = \nu \exp(-E_b^A/kT), \quad (8)$$

where ν is the attempt frequency, typically taken to be $1 - 3 \times 10^{12} \text{ s}^{-1}$, E_b^A is the barrier against diffusion, which depends on the surface chosen, k is the Boltzmann constant, and T is the temperature (K) [36, 47, 59]. Measured examples of E_b^A/k for atomic hydrogen are 287 K for olivine and 511 K for amorphous carbon [47].

The *average* rate of reaction for our single A species is given by the rate of hopping multiplied by the probability that a nearest-neighbor site is occupied by species B, which in turn is given simply by the number of sites occupied by B, $N(B)$, divided by the total number of lattice sites N . Now if we also consider the movement of species B and the fact that there are $N(A)$ species on the grain, we obtain the reactive rate law:

$$dN(A)/dt = -k_{A-B}N(A)N(B), \quad (9)$$

where the rate coefficient is given by the expression

$$k_{A-B} = (k_{hop}^A + k_{hop}^B)/N. \quad (10)$$

This rate law pertains to the case where species A and B can be assumed to react instantaneously upon finding themselves in the same lattice site. If, however, there is a chemical barrier (activation energy) for reaction, an additional term, amounting to the probability of reaction, must be considered. This term, normally referred to as κ , expresses the probability of tunneling under the barrier or climbing over it [36]. The use of such a simple multiplicative term is controversial, with some investigators preferring to consider the actual competition between diffusion out of the lattice and chemical reaction [53].

Including the accretion rate of gas-phase A molecules and the desorption rate of surface A species, and assuming that A only reacts with B, we obtain the total rate law:

$$dN(A)/dt = k_{acc}^A n(A) - k_{des}^A N(A) - k_{A-B} N(A)N(B) \quad (11)$$

where $n(A)$ is the gas-phase concentration of A, k_{acc}^A is the accretion rate coefficient ($\text{cm}^3 \text{s}^{-1}$), and k_{des}^A is the desorption rate coefficient (s^{-1}). The accretion rate coefficient is given by the formula

$$k_{acc}^A = S\sigma v_A, \quad (12)$$

where S is the sticking coefficient, σ is the granular cross section, and v_A is the thermal velocity of gas-phase A. The sticking coefficient can be approximated as unity for low temperature adsorption into sites of physisorption. For chemisorption, on the other hand, in which transmission over a barrier is required, more detailed theories such as transition state theory can be utilized [34]. The desorption rate coefficient depends upon whether we consider evaporation or non-thermal desorption. For evaporation, it is given by the Polanyi-Wigner relation [34]:

$$k_{des}^A = \nu \exp(-E_D^A/kT), \quad (13)$$

where ν is the attempt frequency, and E_D^A is the energy required to desorb A from the surface, often referred to as the binding energy. This energy is in principle determinable by TPD measurements as well as more classical techniques. Recent values (divided by k) determined for atomic hydrogen are 373 K on olivine and 658 K for amorphous carbon [47]. The barrier against diffusion is typically less well known than the binding energy, and is often approximated as approximately 0.30 of the larger energy, although this figure is clearly inaccurate for H atoms on olivine and amorphous carbon, where a ratio closer to 0.8 is appropriate [47]. Even for physisorption, desorption energies for most species heavier than hydrogen are too large for evaporation to occur in cold clouds. For example, a typical energy is around 1000 K (0.1 eV). For a temperature of 10 K and a frequency ν of $3 \times 10^{12} \text{s}^{-1}$, the rate coefficient for evaporation is $1 \times 10^{-31} \text{s}^{-1}$. For H atoms on olivine, on the other hand, this rate coefficient is $2 \times 10^{-4} \text{s}^{-1}$, which is far more significant.

A gas-grain model can be constructed out of rate laws for all species on grains as well as rate laws for gas-phase species, the latter consisting of terms for chemical reactions in the gas, and accretion and desorption terms. Such models have been constructed for the chemistry of cold dense clouds starting from the work of Pickles and Williams [18, 36, 39, 58]. But are rate equations valid for surface species? The basic problem concerns the small abundance per grain of reactive species such as atomic hydrogen. Given the low accretion rate per grain and the rapidity of chemical reactions, the average abundance per grain of such species can be very low, even lower than unity. Such a small average number raises questions concerning its meaning, since after all, grain abundances are discrete entities. Nor is it clear what the meaning of the statistical fluctuation is. So, it is clearly desirable to utilize a method that takes into account both the discrete nature of the problem and statistical fluctuations. Such methods, labeled “stochastic”, concern themselves with the *probability* of finding a certain number of species of a given type on a grain at any time. From these probabilities, average abundances can be obtained. For example, if $P_m(A)$ designates the probability that m molecules of species A are present on a grain, then the average number of species $\overline{N}(A)$ is given by the expression

$$\overline{N}(A) = \sum_{m=1}^{\infty} [m \times P_m(A)]. \quad (14)$$

Similarly the average of the squared abundance can be obtained by the relation

$$\overline{N^2}(A) = \sum_{m=1}^{\infty} [m^2 \times P_m(A)]. \quad (15)$$

so that a standard deviation σ can be calculated from the relation

$$\sigma^2 = \overline{N^2}(A) - (\overline{N}(A))^2. \quad (16)$$

The fact that the upper limit in the sums is formally infinite indicates a potential pitfall of methods that calculate probabilities: they run into trouble when the probability remains large for large numbers of species because there is no guarantee of convergence. Of course, in a situation where the probability is large for a wide range of numbers, it is easier to use the rate equation technique.

Before tackling stochastic approaches, it is important to state that the rate equations can be modified in a semi-empirical manner to mimic some of the results of these methods. The approach, known as the modified rate method, artificially forces the abundances of reactive surface species to be at least unity if necessary by, among other changes, reducing the rate of diffusion of the species to the larger of the accretion and evaporation rates [64]. The approach is easily implemented in gas-grain models [65, 66, 67], and often is in agreement with more detailed approaches as they become available [4, 64].

4.2. Stochastic Methods

We first consider two stochastic methods that are based on the underlying principle that the rate of reaction is related to the product of the hopping rate and the probability of finding a reactive partner in a nearest-neighbor site.

4.2.1. Monte Carlo Approach In the Monte Carlo approach [61, 68, 69], the rates (more strictly the inverse time scales) for adsorption, desorption, and hopping are calculated as in the rate equation approach, and their relative values compared with random numbers after randomly chosen time intervals picked from a standard Poisson distribution $\psi(t)$:

$$\psi(t) = \rho \exp(-\rho t) \quad (17)$$

where ρ is the sum of all relevant rates. Since the average time interval of this distribution is $1/\rho$, the clock is moved up on average by this amount. At the new time, the probability of an individual event happening is equal to its rate divided by the sum of all rates. This probability is compared with a random number to determine which process occurs. For example, if the probability of process (i) to occur is 0.1, it can be assigned to the range of random numbers 0.5 - 0.6 of all random numbers in the range 0-1. If hopping of a given species occurs, another random number is chosen and compared with the fraction of sites occupied by prospective reactive partners to determine whether or not reaction occurs.

Although used for a variety of simple models of surface chemistry in dense clouds in which no gas-phase chemistry is allowed to occur [64], the Monte Carlo approach faces the problem that it is not facile to couple it with a rate equation approach to gas-phase chemistry. The rate-equation approach is based on differential equations that are continuous in time, while the Monte Carlo method advances the time discretely. Another possibility is to use a Monte Carlo method to simulate the gas-phase chemistry [68] simultaneously with the surface chemistry, but technical problems have prevented us from doing such a calculation with current limitations on computational power.

4.2.2. Master Equation Approach In the master equation approach, the *probabilities* are given by kinetic-type equations that relate the time dependence of the probability to gain and loss terms [59, 60, 61, 63]. Let us consider species A once again, but for now consider only reactions between two A species. In place of the rate equation (eq. 11), we have a series of equations for $P_m(A)$ of the type:

$$\begin{aligned} dP_m(A)/dt = & k_{acc}^A n(A) [P_{m-1}(A) - P_m(A)] + \\ & k_{des}^A [(m+1)P_{m+1}(A) - mP_m(A)] + \\ & k_{A-A}/2 [(m+2)(m+1)P_{m+2}(A) - m(m-1)P_m(A)] \end{aligned} \quad (18)$$

To understand this equation, let us consider the case when $m = 2$. On an infinitesimal time scale, only adsorption and desorption of one particle need be considered. The first term on the right is the accretion term: here $P_2(A)$ increases if accretion occurs when one particle is on the grain and decreases when two particles are already there. The second term is the desorption term: here $P_2(A)$ increases if three particles are initially present and decreases if two particles are present before desorption. Note that the rates of desorption must be multiplied by the number of particles present. Finally, the third term on the right is the self-reactive term, where we must consider the number of possibilities for two A species to collide with one another in the same lattice site. Clearly for a positive outcome, we must start with 4 species on the grain. There are then $4 \times 3/2 = 6$ combinations of particles to include. For a negative outcome, we must start with 2 species, and there is only one combination to consider. Although master equations seem to be intuitively correct, they can be derived from the more basic Kolgomorov equation [61].

Solutions of these coupled equations will yield the $P_m(A)$ as functions of time. The average abundance of A and its standard deviation can then be computed. Interestingly, if we consider an analogous equation for the product of reaction, A_2 , and neglect accretion and desorption terms, we can sum up the individual equations after multiplying them by m , and obtain the expression

$$d(\overline{N(A_2)})/dt = k_{A-A}[\overline{N(A)(N(A) - 1)}] \quad (19)$$

which is quite different from a rate equation approach, in which the right-hand side would just contain the square of $N(A)$. Thus, the difference between the two approaches, when the population of A is small, will be significant.

But what happens if we wish to replace equation (11) by a master equation treatment with two types of species? We must then face the fact that the probabilities for specific populations of A and B are coupled together. If we denote the joint probability for m particles of A and n particles of B to be present as $P(m, n)$ and assume that A and B can react only with each other to form AB, we can write the two-body coupled master equation as follows:

$$\begin{aligned} d(P_{m,n})/dt = & k_{acc}^A n(A) [P_{m-1,n} - P_{m,n}] + \\ & k_{acc}^B n(B) [P_{m,n-1} - P_{m,n}] + \\ & k_{des}^A [(m+1)P_{m+1,n} - mP_{m,n}] + \\ & k_{des}^B [(n+1)P_{m,n+1} - nP_{m,n}] + \\ & k_{A-B} [(m+1)(n+1)P_{m+1,n+1} - mnP_{m,n}]. \end{aligned} \quad (20)$$

If both A and B can react with themselves, then two additional terms must be added to the equation. Similarly to the case of A_2 , one can sum the master equation terms for AB in the absence of accretion and desorption of AB to obtain:

$$d(\overline{N(AB)})/dt = k_{A-B} \overline{N(A)N(B)}, \quad (21)$$

showing that there is still a difference with the rate equation treatment, where the averaging of $N(A)$ and $N(B)$ would be done separately.

To use the master equation treatment in a large gas-grain model, one has to divide the types of surface species into two: those that are very reactive (atoms and radicals) and those that are unreactive or weakly reactive [61]. The former will have small surface populations, which must be calculated by stochastic methods, and the latter large ones, for which rate equations can be used. The division into two classes of species is an approximation, the details of which are discussed by Stantcheva et al. [61]. For example, one approximates reactive terms in the master equation for species A with B with terms of type

$$k_{A-B} \overline{N(B)} [(m+1)P_{m+1}(A) - mP_m(A)] \dots \quad (22)$$

if B has a large surface population, in which case the average population of B would be determined by a rate equation. There is still a problem treating the atoms and radicals in the model, however, if there are more than several of them because the multi-body master equation will contain many terms. For example, if there are 10 atoms and radicals to be considered, the master equation will consist of individual equations to determine $P(i, j, k, l, m, n, o, p, q, r)$ where the indices refer to the individual populations of the reactive species. If upper limits of 4 of each species can be imposed in the solution, there are $5^{10} \approx 10^7$ coupled equations to be solved. Even if upper limits of 2 are meaningful, there are still $3^{10} \approx 60000$ coupled equations. It is clearly necessary to make an additional approximation. Two methods have been suggested: (i) a cutoff on the *total* number of species present on a grain at any one time [70], and (ii) a reduction in the amount of correlation needed, so that the dimensionality of the problem can be reduced, or alternatively, the probability can be approximated as a product of smaller, conditional probabilities [71]. Although the first method has now been utilized on a gas-grain model of small size [4], the second method shows promise of eventually permitting a full scale gas-grain chemical model of interstellar cloud chemistry. Nevertheless, to be efficient, a computer code that incorporates the master equation treatment must be able of switching to the rate equation method if the surface population of a species becomes larger than unity on average, because neither method is sustainable if the equations cannot be efficiently truncated at low populations.

How do the two stochastic methods compare? Comparisons on simple systems of surface reactions have been done [61, 70] and show excellent agreement. Moreover, the results of these approaches can differ strongly from those obtained with the normal rate equation method, although the modified rate method is in closer agreement [4, 64].

5. More Detail: H₂ Formation

A detailed comparison between the results of the master equation and rate equation methods has been undertaken for the formation of molecular H₂. To compare the methods, one can define a reaction efficiency η as the ratio of twice the number of H₂ molecules produced on a grain divided by the number of H atoms incident upon that grain within a given period of time [59]. This reaction efficiency is calculated under steady-state conditions, where there is no change in the average atomic hydrogen surface abundance. The stochastic method predicts an asymptotic efficiency for large grain sizes with surface populations of H that exceed one, and this asymptotic efficiency is in agreement with the rate equation result. For smaller grains, however, the rate equation result remains the same while the stochastic efficiency can become much lower [59, 63]. The size at which this discrepancy begins to show up depends on the physical conditions and the energy parameters. If one utilizes the results of [47] for olivine at 10 K, the asymptotic large grain limit ($\eta \approx 0.2$) is reached at a radius of 0.1-1.0 μm with an H atom flux representative of diffuse cloud conditions [59, 62, 63].

The fact that differences appear between the results of stochastic treatments and the standard rate equation treatment does not mean that the former are exactly correct. Indeed, there is a source of error in all of the approaches discussed so far: they are based on an approximate view of how surface reactions occur. The idea that, on average, reactions take place when the hopping of one species takes it into a nearest neighbor lattice site that is occupied by a reaction partner begs the question of what really happens when the two reactants are farther apart. To study the details of how the reactant partners find one another on an individual grain with a low surface population of adsorbates, one must simulate the physical process known as random walk in some detail [62]. In one dimension, random walk is exceedingly inefficient since a species can diffuse backwards to an already occupied site with the same probability as it diffuses forward. In two dimensions, there are more nearest neighbors (4 in a standard rectangular lattice) and the probability is only 1/4 that the previous site will be diffused into. Still, it is well known that

a random walk in two dimensions can result in slowing the pace of reaction by a logarithmic term [72]. One can use a more detailed Monte Carlo approach than the one discussed in section 4.2.1 to actually look at the specific spatial distribution of adsorbates on a surface as a function of time and so simulate random walk and how it affects reaction efficiency. The basic idea is to consider the surface to be a square lattice with $N^{1/2} \times N^{1/2}$ sites, with periodic boundary conditions. Then, as the clock steps forward, one considers the hopping of each individual species, as well as the adsorption and evaporation of others. Reaction is assumed to occur when reactive species land in the same lattice site. The specific procedure used by us to simulate the kinetics of H_2 formation is known as the continuous-time random walk (CTRW) method [73]; here one generally defines time steps for each process rather than for the combined rate of all processes, although hopping and desorption are considered together [62].

Interestingly, the method can be used to study both regular and more complex surfaces, the latter by replacing single energies for diffusive barriers and binding energies by several values or by continuous distributions. The other methods discussed cannot be used to treat continuous distributions.

The results to be discussed below were obtained recently by us [62]; they concern the reaction efficiency for the formation of H_2 as a function of temperature and granular size on assorted surfaces based on the olivine and amorphous carbon results of the Vidali et al. collaboration [47]. A flux of H atoms relevant for diffuse clouds is once again incident upon the grains. It was assumed that H_2 products leave the grain after formation by instant ejection or rapid evaporation. This assumption can be inaccurate only at the lowest temperatures of the simulation where evaporation can be relatively slow. The existence of large numbers of H_2 molecules on the surface can then interfere with the adsorption of additional H atoms. The specific parameters used are shown in Table 3. Note that the flux of H atoms in Table 3 is in units of ML (monolayers) s^{-1} . To convert this into a more normal flux, with units of atoms $\text{cm}^{-2} \text{s}^{-1}$, one multiplies by the surface lattice density s . The number of atoms per second striking a grain of radius r can then be obtained by multiplication by the surface area of the grain.

Table 3. Parameters used in CTRW calculations.

Parameter	Value
H-atom flux	$1.8 \times 10^{-9} \text{ ML s}^{-1}$
ν	$1.0 \times 10^{12} \text{ s}^{-1}$
Lattice type	4 nearest neighbors
Olivine E_b/k	287 K
Olivine E_D/k	373 K
Carbon E_b/k	511 K
Olivine E_D/k	658 K
$\bar{\sigma}$	0.0-0.5
C islands (1.8 %)	15×15
C islands (40 %)	63×63

5.1. Homogeneous Surfaces

The word “homogeneous” here refers to surfaces with single derived values for diffusive barriers and desorption energies for a given adsorbate, in this case atomic hydrogen. The two homogeneous surfaces considered are olivine and amorphous carbon. Some results are shown in

Table 4, in which large grains are those with 316×316 sites, corresponding to a radius of $\approx 0.063 \mu\text{m}$ while small ones contain 1/100 the number of sites and possess 1/10 the radius. Parameters listed for large grains include the temperature of peak efficiency as well as the efficiency η at this temperature, the efficiency at 10 K for olivine, and the temperature ($T_{\eta=0.1}^{up}$) at which η drops to ≈ 0.1 as temperature increases past that of peak efficiency. The parameter listed for small olivine grains is the efficiency at 10 K. In all cases, the reaction efficiency is obtained at steady state, when the abundance of H atoms is constant to within the noise of the approach. At a given temperature, the asymptotic value of η for large grains tends to be somewhat smaller than the master equation/rate equation results, especially when the larger efficiency is not close to unity. The discrepancy can be assigned to the problem of back diffusion because CTRW calculations in which the lattice is changed to one with six nearest neighbors show that η increases to the point that it is only slightly below the master equation result. To be specific, for olivine at 10 K, the asymptotic equation efficiency for the CTRW result with four nearest neighbors (the standard value) is 0.075 and for six nearest neighbors 0.15, still below the master equation value of close to 0.2. As the grain size decreases, the efficiency obtained by the CTRW method decreases. For example, as shown in Table 4, the efficiency at 10 K for olivine grains with $32 \times 32 \approx 1000$ sites, corresponding to a grain of radius of about 6.3 nm, is ≈ 0.04 . This drop is not as steep as calculated by the master equation, so the two methods are actually in agreement for the smallest grains.

The calculated temperature dependence of the reaction efficiency for large grains follows very closely that of the rate equation and master equation approaches. For olivine, the reaction turns on at 5-6 K, has a peak efficiency of near unity at approximately 7.5 K, and turns off at approximately 10-11 K, with the CTRW approach showing a slightly steeper drop-off at high temperatures. For amorphous carbon, the reaction turns on at about 10 K, has a peak efficiency of approximately unity near 13 K, and turns off at 18 K. To be more specific, $T_{\eta=0.1}^{up}$ is 9.9 K for olivine and 17.4 K for amorphous carbon. The reaction operates efficiently at higher temperatures for amorphous carbon because both the diffusive barrier and desorption energy are larger than for olivine. The small temperature range of high efficiency is obtained because at lower temperatures the H atoms cannot move in the absence of tunneling and at higher temperatures they evaporate before reacting at the chosen adsorption flux. These calculated ranges of temperature for both olivine and amorphous carbon are too low to explain the efficient formation of H_2 in diffuse interstellar clouds since it is estimated that dust surfaces are at temperatures near 20 K.

Table 4. CTRW results for homogeneous surfaces.

Surface	Size	Parameter	Result
Olivine	316×316	T_{peak}	7.5 K
		η_{peak}	1.0
		$T_{\eta=0.1}^{up}$	9.9 K
		$\eta(10 \text{ K})$	0.075
Carbon	316×316	T_{peak}	13 K
		η_{peak}	1.0
		$T_{\eta=0.1}^{up}$	17.4 K
Olivine	32×32	$\eta(10 \text{ K})$	0.04

5.2. Inhomogeneous Surfaces

There are several types of surface irregularities, for all of which we will use the term “inhomogeneous.” It is our view that a truly amorphous surface has a continuous distribution of diffusive and binding energies for adsorbates such as atomic hydrogen, and so the term “amorphous” will refer to the use of these continuous distributions, centered around the values determined from TPD experiments. Although detailed calculations have not been performed, it is reasonable to assume that the use of distributions will actually improve the analysis of the TPD data. The previous use of the term “amorphous” for amorphous carbon refers to the actual experimental material, rather than to the model used to fit the TPD spectrum of adsorbed hydrogen atoms. The interaction between atomic hydrogen and amorphous surfaces in our sense will be represented by two continuous distributions: one for diffusive barriers and the other for desorption energies. The distributions are assumed to be correlated, so knowledge of one parameter at a given site yields the other parameter. Two different types of distributions have been utilized: an exponential one and a Gaussian one. Arguments can be made in favor of either distribution, although reality is doubtless more complex. The equation governing the exponential distribution P_{exp} for diffusive barriers is

$$P_{exp}(E'_b) = (T_0)^{-1} \exp(-\frac{E'_b}{T_0}), \quad (23)$$

where T_0 is the average of E'_b , and $E'_b=0$ refers to E_{b0} , the lowest diffusive energy allowed. A normalized variance $\bar{\sigma}$ is defined as $T_0/(T_0 + E_{b0})$. The analogous distribution for the Gaussian case is given by

$$P_G(E_b) = \frac{1}{\sqrt{2\pi}(T_0)^2} \exp(-\frac{(E_b - \bar{E}_b)^2}{2(T_0)^2}) \quad (24)$$

where T_0 is the standard deviation and \bar{E}_b is the average diffusive barrier. The normalized variance $\bar{\sigma}$ is given in this case by the ratio of T_0 to \bar{E}_b . Thus, a normalized variance $\bar{\sigma} = 0.1$ signifies a distribution with an appropriately defined width 0.1 of the average value of the energy. For the exponential case, this means in addition that E_{b0} is 0.9 of the average binding energy, defined to be the same as measured for the homogeneous material. In the CTRW results discussed here, the diffusive barriers and binding energies for each site are determined randomly before the actual reaction begins. For small grains especially, the Monte Carlo treatment of the reaction must be repeated many times to determine appropriate uncertainties since different individual lattices show very different patterns of lattice site energies. Another approach, which does not allow a determination of the uncertainty, is to redetermine the binding and diffusive energy for each site whenever a new H atom enters the site.

It is unfortunate that there are few if any useful estimates on the value of $\bar{\sigma}$ for amorphous surfaces. Some calculations have been done for binding energies of H on amorphous ice [74], and some measurements will soon be available for this surface from the Danish group (Hornekaer et al., in preparation). The scant amount of evidence suggests that values of $\bar{\sigma}$ as high as 0.2 are not unreasonable, but it is not clear that significantly higher values exist for surfaces such as olivine and amorphous carbon. Nor is it clear that the distribution of energies is either exponential or Gaussian. Nevertheless, we have performed calculations for $\bar{\sigma}$ as high as 0.5. For values this large, the exponential distribution is to be preferred because there is a danger of negative energies occurring for the Gaussian distribution.

For large grains, our results for amorphous olivine and carbon show that the greater the value of $\bar{\sigma}$ the more efficient the reaction and the higher the range of temperatures for which it is reasonably efficient. Table 5 shows results with exponential distributions. For amorphous olivine, $T_{\eta=0.1}^{up}$ increases from 10 K to 12 K and, for amorphous carbon, increases from 17 K to 22 K when $\bar{\sigma}$ goes from 0.0 to 0.1. If $\bar{\sigma}$ is increased to a rather large value of 0.5, $T_{\eta=0.1}^{up}$

increases dramatically to 20 K for olivine and 35 K for carbon. These latter values show that strongly inhomogeneous large grains represent reasonable sites for the efficient formation of H_2 in diffuse clouds. The reason that the range of temperatures for efficient reaction extends to much higher temperatures is that the sites of large binding/diffusive energy hold their H atoms tightly so that faster-moving H atoms can still find and react with them at the higher temperatures. Note that the whole distribution of efficiencies does not move towards higher temperatures; the efficiencies at lower temperatures are not much changed from the homogeneous case and, in any case, are not reliable because of the problem of H_2 remaining on the surface and the possibility of reactions occurring via the Eley-Rideal mechanism. For smaller grains, the calculations show that the efficiency decreases, but less significantly than for homogeneous surfaces. The smaller the lattice, the larger the uncertainty given the wide variation in energies among the small number of lattice sites. One eventually approaches a limit in which the small grains are better understood as individual and distinctive molecular species.

Table 5. CTRW results for large inhomogeneous surfaces with exponential distributions.

Surface	Size	$\bar{\sigma}$	$T_{\eta=0.1}^{up}$ (K)
Olivine	316×316	0.1	12
		0.5	20
Carbon	316×316	0.1	22
		0.5	35
Olivine-Carbon (40%)	316×316	0.0	16
		0.2	24
		0.5	30

A second type of inhomogeneity refers to mixed, composite surfaces of olivine and carbon. The calculations reviewed here were done with islands of carbon placed randomly onto an olivine lattice, with sizes depending on the percentage of carbon listed in Table 3. Calculations have been undertaken for mixed surfaces in which both the olivine and carbon are homogeneous, and in which the carbon is truly amorphous; that is, has a continuous distribution of diffusive and binding energies. Some of the results are shown in Table 5 for surfaces with 40 percent carbon organized into islands (see Table 3). It can be seen that the range of temperatures increases as $\bar{\sigma}$ increases. Although not shown in the table, the results show broad distributions extending from the lowest temperatures for efficient formation on homogeneous olivine (6 K) upwards.

A third type of inhomogeneity refers to surfaces with imperfections such as kinks and terraces, at which the binding energy is significantly greater than in a normal site. Surfaces with significant numbers of such irregularities are referred to as “rough”. Preliminary calculations show that rough surfaces show very similar effects to amorphous surfaces in increasing the range of temperatures over which H_2 formation is highly efficient. It would thus seem that the problem of efficient H_2 formation in diffuse interstellar clouds can be understood in terms of large inhomogeneous grains, although supporting laboratory experiments and analyses would be most welcome.

6. Photon-Dominated Regions

Photon-dominated regions (PDR’s) are portions of interstellar clouds that are close to stars and so are warmed by high levels of photons [75, 76]. Given that large numbers of stars are

formed in giant molecular cloud complexes, PDR's are ubiquitous in the interstellar medium. Perhaps the most picturesque is the so-called horsehead nebula in Orion, where the dark head of a horse is silhouetted by reddish radiation from a nearby bright star. Another famous one is the Orion Bar, in the same constellation. Here a group of very bright stars (the Trapezium stars) have lit up the area around them like a Christmas tree. The bright environment is known as an HII region, since all molecules have been dissociated into atoms and ionized to form a high-temperature plasma. But molecules are hardy beasts. Right at one of the borders of the Orion HII region (also called the Orion Nebula and visible to the naked eye in the winter sky) starts the well-studied PDR known as the Orion Bar.

The standard PDR model is a one-dimensional system in which slabs of differing temperature and density are considered, starting from the outside with low densities and high temperatures and proceeding to the inside with lowering temperatures and increasing densities. As one traverses inward, the dominant species change once the chemistry is evolved. For example, if we consider the major forms of carbon: the outer layers are dominated by C^+ , the inner layers by CO, and some intermediate layers have significant amounts of neutral atomic carbon. Hydrogen is atomic in the outer layers, but a short distance inward is normally sufficient to witness an efficient conversion to the molecular form. Common to all PDR models, whether they are for diffuse or dense gas, is a careful treatment of radiative transfer through the cloud, especially for the molecules H_2 and CO, which to a significant extent manage to shield themselves from external radiation. The H_2 shielding occurs because of an unusual mechanism for photodissociation in which absorption to specific vibrational states of a bound, excited electronic state is followed by emission into the continuum of the ground electronic state. Thus, the radiation field is soon bereft of the specific wave lengths needed for photodissociation. The shielding is of course coupled with the chemistry since it requires a significant amount of the molecule. At present, most PDR models include only gas-phase chemistry in any detail and make the untenable assumption that any H atom that hits a grain will convert to H_2 with unit efficiency.

To obtain a better estimate of the efficiency of formation of H_2 in PDR's, it is necessary to look at the surface chemistry in some detail. Although temperature estimates differ, a useful range of surface temperatures in known PDR's extends from a low of perhaps 20 K to a high of perhaps 100 K, depending of course on factors such as the proximity to the star and the intrinsic brightness of the star [77]. The gas temperature can be considerably higher than the grain-surface temperature; estimates of up to 1000 K have been made [78]. If one looks at the results of our CTRW calculations on inhomogeneous materials, it is probably a stretch to suggest that our materials are useful surfaces for H_2 formation, especially in the warmer PDR's. The model of Cazaux & Tielens [49], which includes chemisorption sites that are accessible without significant activation energy, does show reasonable efficiencies from low surface temperatures through temperatures much higher than pertain to PDR's. Even if a more standard model is undertaken, in which entrance into chemisorption sites requires overcoming a barrier, it is still possible that the gas-phase temperatures are sufficiently high for this to occur. For a graphite-like barrier E_a of 0.2 eV, a temperature of 1000 K leads to a Boltzmann factor $\exp(-E_a/kT)$ of $\exp(-2.3) = 0.1$ so that even in the absence of tunneling, a significant fraction of H atoms will be able to undergo chemisorption. Subsequent reactions to form molecular hydrogen may occur predominantly through an Eley-Rideal mechanism [77, 79]. Calculations to test this mechanism are planned. The efficiency on small grains, especially on PAH's [10], may be reduced by the flux of hard ultra-violet photons, which can stochastically heat these particles to high enough temperatures to desorb even the chemisorbed H atoms [80]. Detailed calculations are necessary to compare the rate of desorption, best handled by unimolecular decay theory [81], and the rate of cooling by radiative relaxation.

7. Conclusion

The challenges facing investigators of the chemistry that occurs on the surfaces of interstellar grains are daunting. Yet much progress is being made. Experimental investigations have confirmed the ideas of astrochemists that molecular hydrogen is formed efficiently on cold grains, and that a variety of other reactions leading to saturated species such as methane, ammonia, water, and even methanol occur. We are not yet at the stage where the results of experiments can be unambiguously interpreted and used to calculate rates for interstellar clouds, but even here progress is being made. Older chemical models, in which surface reactions were treated with rate equations, are giving way to more accurate treatments, in which the stochastic nature of the process is incorporated. Still to be included in detailed gas-grain models are the effects of grain size distribution and surface inhomogeneities, although these are being studied for the simple case of the single reaction to form H_2 . Further advances will undoubtedly require less ambiguous experimental results, preferably obtained directly on small particles [82], as well as more efficient stochastic approaches for large-scale models.

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8. References

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