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Grain Formation Modulated by Molecular Hydrogen Evaporation in the Interstellar Medium†

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A mechanism for grain growth and formation in the interstellar medium is proposed. In this mechanism, hydrogen molecules act as moderators. The process begins when they physisorb to the surface of the grain. Then, when a collision with a heavy atom occurs, the bonding energy is carried away by the evaporation of hydrogen molecules. Estimates are made of the number of hydrogen molecules bound to the surface of a grain that would be sufficient to facilitate this mechanism at 13 K for amorphous carbon and 8 K for a silicate grain.

1. Introduction

Grains in the interstellar medium (ISM) play a critical role in the physics and chemistry in interstellar space. These interstellar grains are submicrometer particles which absorb and reradiate photons and are the main cause of dark patches in the night sky. Grains are almost certainly involved in the dominant mechanism yielding hydrogen molecules.[1] Understanding the mechanism of formation of these grains is important to our explanation of astrophysical and astrochemical processes at the atomic level in the ISM. This paper proposes a simple mechanism by which interstellar grains may be formed specifically in the ISM.

One accepted mechanism for the formation of interstellar grains is their nucleation and growth in outflows of red giants and red supergiants,[2−4] and also in the ejecta of supernovae.[5] Supernovae also cause violent shocks in the ISM, which provide the primary destruction mechanism of the grains.[6−8] The shock waves preferentially heat the atoms surrounding the grains, resulting in large relative velocities between the grains and the surrounding gases. The high velocity gases lead to sputtering of the grains, and eventually to grain−grain collisions which further shatter the grains.

Estimates using the rate of occurrence of supernovae, and the effect of the resulting shockwave suggest that an interstellar grain should be returned to the gas phase on a time scale of approximately 5×10^8 years,[6−10] while the injection of newly condensed grains has been estimated to occur on a time scale of $\sim 3 \times 10^9$ years. Slavin et al. have suggested that part of this discrepancy is due to an overestimate of the rate of grain destruction in the existing models.[11] Nevertheless, the two estimates would suggest that relatively few of the grains would be observed. Instead, interstellar grains are ubiquitous,[12] strongly suggesting that some additional process for grain formation or recondensation is occurring.

Here, we propose an additional process that could be generating grains. The mechanism we envision begins when several hydrogen molecules physisorb to a small grain or single heavy atom. After a period of time, a heavy atom collides with the cold cluster of hydrogen molecules, which presumably contains a heavy atom responsible for its nucleation, at an energy low enough that the incoming heavy atom also physisorbs to the cold cluster. The cluster then rearranges to form a heavy−heavy bond, immediately after which some or all of the excess energy released by the bond formation is carried off by evaporating hydrogen molecules. This provides an effective alternative process to phonon excitation in the grain, for dissipating the bond energy.[13,14] Hydrogen molecules may then slowly reattach and rebuild a larger cluster, which can again be hit by a heavy particle, followed by massive evaporation. This process may continue indefinitely, with the hydrogen molecules acting as moderators to enable slow, steady accumulation of the heavy atoms.

In this paper, we present some basic calculations determining conditions under which this mechanism is plausible. There are many uncertainties, so this should be considered simply as opening a door to a mechanism that seems worthy of further investigation. The calculations are sensitive to the physisorption barrier of the hydrogen molecules, the temperature of the grains, the density of hydrogen molecules and heavy atoms in the ISM, and the sticking coefficient of the hydrogen molecules on the surface of the grain. Some of the parameters necessary to test this proposal rigorously are not yet available; this presentation should be thought of as a proposal plausible enough on the basis of current information to make it worth investigating.

2. Results

An estimate of the number of hydrogen molecules physisorbed to the surface of a typical interstellar grain between collisions with a heavy atom has been made using experimental data on the conditions likely to be found in a giant molecular cloud and associated physical constants. This allows for an estimate of the energy removed from the grain by evaporation. A discussion of the appropriate conditions and physical constants follows.

The calculation has been performed by using the equation for the desorption of H_2 on a grain surface given by Katz et al.[15]

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$$\frac{dN}{dt} = \nu[H_2] \exp \frac{-E_d}{k_b T} \quad (1)$$

ν is an attempt rate we take to be 10^{12} s^{-1}, E_d is the activation energy barrier for desorption of a H_2 molecule, k_b is the Boltzmann constant, and T is the temperature of the grain. In the experiments of Pirronnello et al.,[16−18] a model grain surface was irradiated with a beam of H and D atoms and HD molecules were produced. A temperature scan was performed, and the results were analyzed in terms of rate equations. The surfaces studied, olivine $(Mg,Fe)_2SiO_4$ and amorphous carbon, show desorption barriers of 27.1 and 46.7 meV, respectively. These data were used to determine the lifetime of the H_2 physisorbed to the grain. The bonding energies for a variety of relevant bonds are found in Table 1.

The sticking coefficient of hydrogen molecules on interstellar grains is another parameter to which this calculation is sensitive. Leitch-Devlin and Williams have calculated this sticking coefficient at a variety of temperatures.[14] In fact, they find that the sticking coefficient rises with grain temperature, as phonon excitation becomes more likely to absorb the kinetic energy of the collision. On a graphite surface, they find a sticking coefficient of 0.2−0.4 for a cold grain, while for a silicate surface the coefficient is 0.03−0.05. The sticking coefficient determines the maximum number of molecules likely to attach between heavy atom strikes. The relevant sticking coefficients are contained in Table 2.

A great variety of conditions may be encountered in the interstellar medium. Conditions range from hot ionized gases near hot young stars in H(II) regions[19] to cold clouds of molecules as found in giant molecular clouds (GMCs).[20] The model proposed here requires low temperatures; otherwise, the physisorbed H_2 will detach too quickly to allow the accumulation of H_2 molecules on the growing grain.

Inferring temperatures from measurements of GMC are nontrivial. Even a precise measurement along a given line of sight is likely to be an average over a variety of temperatures at different depths within the cloud. Bergin et al. have measured the temperature in diffuse molecular clouds (DMCs) using the rotational spectrum in CH_3C_2H; they measure average temperatures along a line of sight as low as 12 K in the dense molecular cores in both Orion and M17, although they observe and stress the complexity of the temperature profile observed.[21] Other measurements use the CO spectrum and suggest that the typical temperatures of some clouds vary between 15 and 25 K.[35] Furthermore, Bergin et al. find that the H_2 density ranges between 3×10^6 and 5×10^6 cm^{-3}.[21] Hence, the interpretation used here is based on a temperature range of 10 to perhaps 30 K, although no explicit value is needed for the model.

Figure 1 shows the calculated extent of H_2 attachment to an amorphous carbon grain after 550 collisions with H_2, cf. Table 3, the approximate average number of collisions of a grain with H_2 molecules between collisions with a heavy atom. The ratio of hydrogen atoms to heavy atoms is roughly constant.[22] We assume that 60% (by mass) of the available hydrogen in the cloud is molecular.[22] The temperature and density were also used to determine the mean free path of the H_2 molecules. This figure assumes that the grain and surrounding gases are at similar temperatures, which need not be the case. The longer the time between heavy atom collisions, the more likely that the H_2 will spontaneously desorb. An approximate cross section of 10^{-15} cm^2 was used.[23,24] Figure 1 shows a maximum density of 160 hydrogen molecules, which corresponds to 7.5 eV of evaporation energy, assuming that the cluster is only a H_2 monolayer. A maximum number of H_2 molecules will attach to the grain at temperatures below 13 K for the high range and 12 K for the low range of densities expected in a giant molecular cloud, and might prove effective at up to 14 K for higher density clouds. The dependence on density is relatively weak, suggesting that the proposed process is applicable at a wide range of densities. This suggests that this mechanism is likely to be effective for very cold parts of molecular clouds based on the binding constants of amorphous carbon.

Figure 2 displays a comparable calculation using the binding constants for olivine. In this case, in order for the molecular attachment to occur at sufficient densities, the temperature must approach 8 K. This temperature is somewhat lower than what has been measured in a giant molecular cloud, although it is conceivable that some pockets of the cloud may be this cold. The fully attached cluster has an evaporation energy of ∼0.75 eV. While this energy is not enough to fully absorb the bond energy, it may leave the small cluster in a stable excited state which may either de-excite radiatively or through further

TABLE 1: Relevant Bond Energies and Energies for Physisorption of H Atoms and H_2 Molecules to Grain-Like Surfaces[15]

H desorption (olivine)	32.1 meV[15]	H_2 (olivine)	27.1[15]
H desoprtion (amorph. C)	56.7 meV[15]	H_2 (amorph. C)	46.7 meV[15]
C−C bond (diamond)	3.67 eV[32,33]	C−C (graphite)	4.92[32]
Si−Si bond	3.38 eV	Si−C	4.68 eV

TABLE 2: Sticking Coefficients for H and H_2 on Model Grain Surfaces[a]

particle	T_{grain} (K)	T_h[34] (K)	sticking coeff.
H	10	10	1.00
H_2(C)	100	10	0.4[14]
H_2(C)	3	10	0.2
H_2(Si)	3	10	0.03[14]
H_2(Si)	3	75	0.05[14]

[a] (C) indicates graphite and (Si) a silicate surface. T_h is the temperature of the gas.

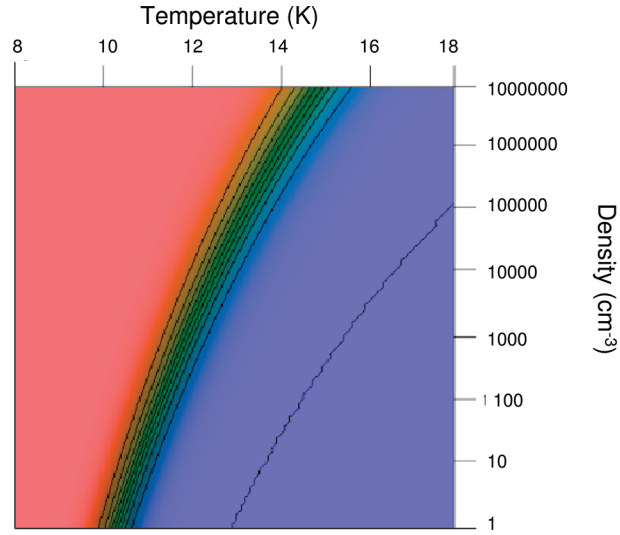

Figure 1. Plot of the estimated number of hydrogen molecules physisorbed to the grain after 550 collisions with molecular H_2, as a function of density and temperature. The desorption barrier is taken to be 46 meV, the H_2 sticking coefficient is 0.3, and the H_2 mass ratio is 0.6. This parameter choice corresponds to a model amporphous carbon grain. The maximum attached is 160 molecules and the minimum is zero, with a difference of 18 H_2 molecules between each contour line. Red indicates 160 H_2 molecules physisorbed, and blue indicates no physisorbed H_2.

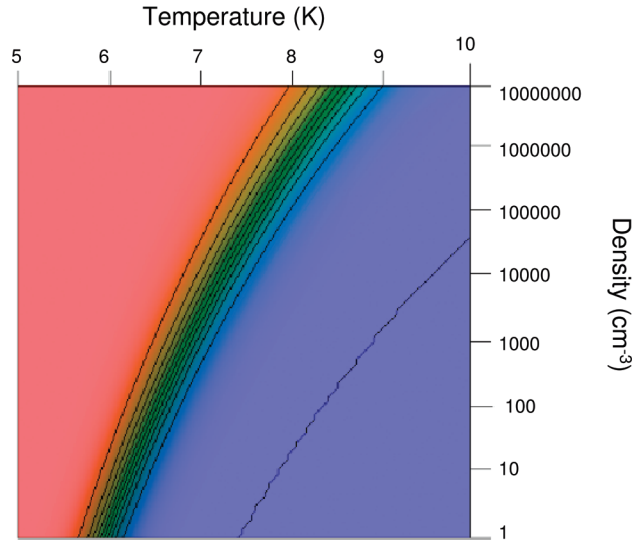

Figure 2. Plot of the estimated number of hydrogen molecules physisorbed to the olivine grain after 550 collisions with molecular H_2, as a function of density and temperature. The desorption barrier is taken to be 27 meV, the H_2 sticking coefficient is 0.05, and the H_2 mass ratio is 0.6. This parameter choice corresponds to a model silicate grain. The maximum attached is 27 molecules and the minimum is zero, with 3 H_2 between each contour line. Red indicates 27 H_2 molecules physisorbed, and blue indicates no physisorbed H_2.

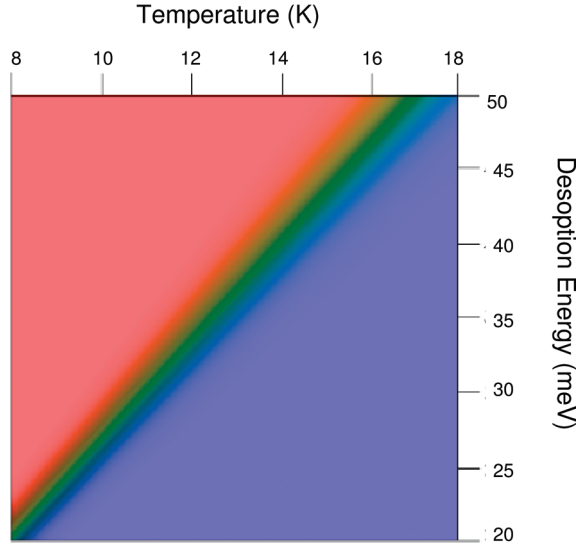

Figure 3. Plot of the estimated number of hydrogen molecules physisorbed to the olivine grain after 550 collisions with molecular H_2, as a function of desorption energy and temperature. The H_2 density is 1×10^6 molecules/cm^3. The H_2 sticking coefficient is 0.05, and the H_2 mass ratio is 0.6. The maximum attached is 27 molecules and the minimum is zero, with 3 H_2 between each contour line. Red indicates 27 H_2 molecules physisorbed, and blue indicates no physisorbed H_2.

collisions. Furthermore, the desorption energy for H atoms is slightly larger than that for H_2 and therefore grain growth may occur at slightly higher temperatures with atomic hydrogen.

Figure 3 plots the number of H_2 molecules physisorbed to the grain surface as a function of the desorption barrier. Because the composition of interstellar grains is not well-known, it would not be surprising for heterogeneous grains with variable composition to exist. This figure shows a roughly linear dependence between temperature and desorption barrier, with a 85 meV barrier allowing the mechanism to work up to 26 K, while at 10 meV the mechanism is feasible at 3 K. This indicates that the desorption barrier and temperature are the most important variables on which this mechanism depends.

The H_2 evaporation mechanism for interstellar grain growth appears to be reasonable for amorphous carbon grains inside giant molecular clouds. The main requirement for this mechanism is that the surface of the grains be cold enough that the weak physisorption holding the H_2 together is not overcome. Also, the sticking coefficient is critical. The sticking coefficient is closely related to the phonon energy levels and depends on the efficiency of kinetic energy transfer into excitation of the grain vibrations. This indicates that a deeper understanding of the H_2 and H atom interaction with the grain is desirable.

While we have focused on grain growth, grain formation is equally interesting, if not more so. While a cluster of a single heavy atom with nH_2 molecules may allow for the formation of an interstellar heavy dimer, the sticking coefficient of H_2 molecules to a single heavy atom and physisorption barrier are not well-known. Instead of resolving this question, the purpose of this paper is merely to propose grain growth via an evaporative mechanism of H_2 molecules. We simply wish to show that such a mechanism is plausible enough to investigate the extent to which it reasonably contributes to the rich chemistry and physics found in the interstellar medium.

Several issues should be explored in the next steps to pursue this mechanism. One is the issue of the kinetics of the energy dissipation from a newly formed bond between a newly arrived heavy atom and either a hydrogen molecule or another heavy atom. From the simulations by Cheng and Landman,[25] it is reasonable to expect that the weakly bound hydrogen molecules will evaporate rapidly, carrying off the bond energy, but this will need to be examined. The grains, at least when they reach moderately large sizes, seem to have very "fluffy" or defective outer structures,[26] which could affect such kinetics. A second issue related to kinetics may be the relative (and absolute) rates of radiative cooling vs cooling by evaporation, and, of course, accompanying the evaporation is the sticking probability for an impinging particle.[27] Naturally, this analysis will require knowledge of the sticking probabilities of hydrogen molecules at the low temperatures of interstellar clouds, probabilities which are not yet well established. Because the effective temperatures relevant for hydrogen-modulated grain growth may not be constant, it may be useful to introduce methods based on temperature control of small particle relaxation[28] or of their desorption,[29] specifically via simulations (although temperature controlled deposition or TPD has been primarily used as an experimental tool for surface studies, as in catalysis).

One further consideration that will surely be quite important in developing an understanding of grain formation and probably of grain growth as well is the difference in behavior of *ortho*- and *para*-hydrogen molecules, and of the corresponding forms of molecular deuterium as well. This has been recognized in the study of van der Waals complexes of molecular hydrogen with the OCS molecule.[30]

3. Conclusions

We have proposed a mechanism that allows for grain growth in the interstellar medium. In this process, a number of H_2 molecules physisorb to the grain, and build up over time. Eventually, a heavy atom collides with the grain,[38] (see Table 3) and the excess bonding energy is carried off by the evaporation of the H_2. This mechanism is most likely to be effective in dense molecular clouds, where Savage and Sembach have shown that about 30% of the Si is locked up in a more loosely bound grain, with an attachment energy of ~2 eV rather

TABLE 3: Interstellar Gas Phase Abundances of a Variety of Atoms with Respect to 10^6 H Nuclei[a]

C	135[40]	Si	18.8[41]
N	75[37]	O	319[36]

[a] This does not include the atoms incorporated in grains.

than the usual ~5 eV.[31] Radiation may well dislodge the physisorbed hydrogen molecules, reducing the feasibility of the mechanism in more exposed regions in the interstellar medium.[39] The proposed mechanism is reasonable in the case of amorphous carbon. H_2 accumulation should occur at temperatures below ~14 K based on the density measured in giant molecular clouds. At lower temperatures, ~8 K, grain growth should occur for olivine, a model silicate surface. While this is rather low compared with measured temperatures, uncertainty in the temperature and desorption barrier cannot rule out the possibility here as well. Furthermore, we have focused only on physisorption of molecular hydrogen. If chemisorption is also included, this provides an additional method of dispersing bond energy. The proposed mechanism may contribute to grain growth and help to explain the surprising ubiquity of interstellar grains. The mechanism will require considerable further investigation to establish the feasibility of this mechanism.

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