

*Formation of Molecular Hydrogen in Interstellar Space*¹

H. F. P. KNAAP, C. J. N. VAN DEN MEIJDENBERG,
J. J. M. BEENAKKER, and H. C. VAN DE HULST
Leiden University
Leiden, The Netherlands

ALTHOUGH SEVERAL ATTEMPTS at observing the interstellar hydrogen molecules in the ultraviolet or infrared are in preparation (ref. 1), these molecules are still undetected. They may form the most abundant unobserved constituent of the interstellar gas. The strongest indirect argument for the presence of these molecules lies in the fact that the density of atomic hydrogen observed by the 21-cm line goes down in some dark clouds, where the dust density and, presumably, the total gas density goes up by a large factor.

Inasmuch as the density in the interstellar clouds is of the order of 10 atoms/cm³ and the temperature is only of the order of 100° K, any formation of molecules by atom-atom collisions is too slow to be of importance. The most eligible process for H₂ formation is recombination on the surface of an interstellar dust grain. Rate estimates of this process have been made in various degrees of detail, as reported in references 2 to 4. The case in which the atoms are bound to the grain surface by van der Waals forces, that is, by physical adsorption, is examined in these references. The binding at the surface then must be of such a type that two atoms can reach each other by surface mobility within the residence time on the grain surface, or before evaporation. In reference 4 it is pointed out that a large surface mobility, independent of temperature, exists as a consequence of quantum-mechanical barrier penetration (tunneling). A conversion time shorter than 10⁸ years is found. However, some aspects of the problem are overlooked, and thus this conclusion may be wrong. Results presented herein show that physical adsorption of atoms on grains of the type proposed in reference 2 does not provide efficient conversion into hydrogen mole-

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cules within the age of the galaxy. The possibility of other, more efficient, models based on chemical absorption remains open.

RECOMBINATION BY PHYSICAL ADSORPTION

† A Lennard-Jones interaction potential is assumed as follows:

$$\phi(r) = -4\epsilon \left[\left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right] \quad (1)$$

where ϵ and σ are constants and r is the distance between an H atom and any molecule of the grain surface. In view of the composition of the grains as proposed by van de Hulst, the quantity ϵ/k , where k is Boltzmann's constant, will have values between 60° K and 100° K, the latter value corresponding to the interaction with H_2O . By summing up the pair interactions the total potential energy of a single H atom can be calculated as a function of the position of the H atom with respect to the solid lattice. The minimum potential energy is then found to be $\phi_{\min} = -6\epsilon$. (See ref. 5.) Classically the adsorption energy would be equal to $|\phi_{\min}|$. Here the first deviation from the treatment of reference 4 occurs. According to quantum mechanics theory, the zero-point energy for a light particle restricted in space is appreciable. As a result, the adsorption energy for the H atom is significantly smaller than $|\phi_{\min}|$. Under the conditions mentioned previously, the adsorption energy of an H atom at the grain surface is reduced from its classical value of 6ϵ to below 2.5ϵ . (See refs. 6 to 8.) A similar situation arises for the analogous problem of the heat of evaporation of a three-dimensional solid. Here the classical value for the heat of evaporation is 8.7ϵ . For light molecules, as, for example, H_2 and He, the heat of evaporation is reduced to 2.5ϵ and 0.7ϵ , respectively.

The following notation and numbers are assumed:

q_a adsorption energy, 2.5ϵ

ν_0 vibration frequency perpendicular to surface, $10^{12}/\text{sec}$ to $10^{13}/\text{sec}$

T temperature of grain, arbitrary

S surface area of one grain, 10^{-8} cm^2

N number density of H atoms in cloud, $10/\text{cm}^3$

T_g temperature of gas of H atoms, 100° K

V average velocity of H atoms at this temperature, $1.45 \times 10^5 \text{ cm/sec}$

α sticking coefficient, $1/3$

τ average residence time of an atom on a grain, $\frac{1}{\nu_0} \exp\left(\frac{q_a}{kT}\right)$ (2)

The justification for the numbers chosen is as follows: The sticking coefficient is experimentally found to be between 0.1 and 1.0 (refs. 9 and 10). The gas density is that often adopted for an average cloud. The average density near the galactic plane is much smaller, about

0.5/cm³. The reason for employing the larger value is that the mean free path of the atoms between gas-kinetic collisions is small. An atom once present in a cloud of this density would move by diffusion not farther than 1 parsec in 10⁹ years, so that it is released from the cloud only if the cloud itself expands or dissolves, which may occur in 10⁷ or 10⁸ years. Hence it seems appropriate to maintain the high density estimate during the entire time considered.

The gas temperature is chosen between the usually adopted 130° K and the lower values which may occur in dense clouds. The surface area of a grain follows from the best single-diameter fit to the extinction curve, which gives a diameter of 0.6 μ. Refinement by a distribution of grain sizes (refs. 2 and 3) gives at most a correction by a factor 2 in the conversion rate. The characteristic frequency ν_0 depends on the precise structure of the surface and can in any model be derived from the shape of the potential well.

A necessary condition for recombination is that during the time an H atom spends at the surface a second one arrives. This requires

$$\tau > (\alpha N V S)^{-1}$$

or

$$T < T_{max}$$

where

$$T_{max} = \frac{q_a}{k} \left(\ln \frac{\nu_0}{\alpha N V S} \right)^{-1} = 4.5^\circ \text{ K to } 7.5^\circ \text{ K} \quad (3)$$

A change by a factor of 100 in any of the quantities under the logarithm introduces a change of about 10 percent in T_{max} . The remaining uncertainty is fully in q_a . For temperatures above T_{max} , the probability of finding two atoms on the same grain is approximately

$$\frac{\alpha N V S}{\nu_0} \exp \left(\frac{q_a}{k T} \right) \approx 10^{-15} \exp \left(\frac{q_a}{k T} \right) \quad (4)$$

Already for $T = 1.1 T_{max}$ the number of grains with two atoms is reduced by a factor 50 and the consequent average recombination time prolonged to 10⁹ years. It may therefore be concluded that at the grain temperatures usually assumed, that is, 10° K to 20° K, the recombination mechanism based on physical adsorption of H atoms on the grain surface is completely ineffective.

The reason that this result deviates from the conclusion reached in reference 4 is twofold: (1) the effect of zero-point energy on q_a was not accounted for in reference 4, and thus q_a is reduced by a factor 2.4; and (2) it was implicitly assumed in reference 4 that an H atom by surface mobility could go on scanning an infinite area for the possible presence of other H atoms, whereas, in fact, the scanning area is limited to the surface of one grain.

FINAL REMARKS

The situation in the physical adsorption model is more favorable for deuterium atoms than for H atoms. Because the zero-point energy is smaller for the heavier D atoms than for H atoms, the adsorption energy for D atoms is larger.

Hence, D atoms will be adsorbed for longer times. From equation (3) is found a value of 10° K for T_{max} for HD formation; this value is larger than the value of T_{max} for H_2 formation. Therefore, if the grain temperatures were low enough for the process to work at all, selective disappearance of atomic D with respect to atomic H would occur and thus preferential formation of HD would result.

Although, at the actual grain temperature, physical adsorption provides an insufficient basis for the recombination of H atoms, a recombination process based on more complicated models is not ruled out. For example, a combination of physical and chemical adsorption might work quite well. Consider a grain with a number of sites on the surface where an H atom is chemically more or less permanently trapped; then the grain is virtually always occupied with H atoms. A physically adsorbed atom can reach a chemically adsorbed atom by surface migration before evaporation. As pointed out in reference 4, the surface mobility of a physically adsorbed atom is quite large because of quantum-mechanical tunneling. The proposed type of traps on the grain might result from radiation.

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DISCUSSION

Harteck: Are these theoretical or experimental results?

Knaap: Theoretical.

Harteck: For interstellar grains of a metal oxide, the absorption may be less for a water layer, or for oxygen, nitrogen, or carbon; but hydrogen atoms still should not act like a noble gas with mass 1.

Knaap: That is true. The absorption depends on whether the substrate is H_2 or water. It might be that H atoms are chemically trapped with sufficient mobility to reach each other on the surface.

Harteck: How do you suppose there would be a layer of hydrogen molecules on the surface? At 7° K the hydrogen would have evaporated.

Knaap: This is not necessarily true, because there is a balance between incoming H atoms and evaporating H_2 molecules. H atoms hit the surface, H_2 is produced, and subsequently H_2 molecules have a chance of evaporating ($\sim \exp(-q_a/kT)$). Hence, the chance of having a layer of hydrogen molecules depends on the amount coming in, the formation rate of molecules, and the number of molecules evaporating.

Harteck: But suppose I had solid hydrogen. The temperature still cannot be 6° K or 7° K.

Knaap: Certainly it would evaporate, if no new molecules were condensed or formed on the surface. That would even be true at a much lower temperature of, for example, 2° K, if one would wait long enough.

Harteck: The heat of evaporation of hydrogen is 204 calories; the heat of fusion is almost 84 calories. You have almost the heat of sublimation, or 304 calories. So you can see at 1° K or 2° K it never evaporates. There is a critical temperature for the density of hydrogen atoms in interstellar space where they cannot remain. I cannot remember the number but I think it is 5° K or 6° K. But at 2° K evaporation would never occur.

Knaap: The interaction energy of the H atom with the solid is obtained by placing the H atom above a crystal. For a number of positions of the H atom the distances to the atoms or molecules of the crystal are calculated. By summing the energies of all binary interactions the total interaction energy is obtained. This has been done with a computer for several positions of the H atom, and -6ϵ was found to be approximately the minimum potential energy of the H atom.

Donn: I think the possibility of experimentally studying these problems using molecular beam techniques is worth mentioning. It has been found that a very low hydrogen recombination probability exists except near 20° K, and that the anomalously large values there may have been caused by the condensation of water vapor to produce an ice coating. I think such experiments, carefully designed to study astrophysical problems, could furnish important data.

Knaap: Unfortunately, no direct experimental results are available. The experiments of Brackmann and Fite are not conclusive as to the absorption rate of H atoms.