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FORMATION OF MOLECULAR HYDROGEN IN INTERSTELLAR SPACE

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It is shown that H-atoms adsorbed at the surface of solid grains by Van der Waals forces (physical adsorption) are loosely bound because of their zero-point energy. Any grain temperature above 8 °K makes the chance of simultaneous presence of two adsorbed H-atoms on the grain too small for efficient recombination. The situation is more favourable for formation of HD and for grains permitting local chemical adsorption.

1. Introduction

Although several attempts at observing the interstellar hydrogen molecules in the ultraviolet or infrared are in progress (see review by Varsavsky, 1965), 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.

As the density in the interstellar clouds is of the order of 10 atoms per cm^3 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 likely process for H_2 formation is recombination on the surface of an interstellar dust grain. Rate estimates of this process have been made in various degrees of detail by Van de Hulst (1948), McCrea and McNally (1960) and Gould and Salpeter (1963).

The latter authors work out the case in which the atoms are bound to the grain surface by Van der Waals forces, i.e. by physical adsorption. The binding at the surface must then be of such a type that two atoms can reach each other by surface mobility within the residence time on the grain surface, i.e. before evaporation. Gould and Salpeter point out that a large surface mobility, independent of temperature, exists as a consequence of quantum-mechanical barrier penetration (tunneling). They arrive at a conversion time shorter than 10^8 years. However, they have overlooked some aspects of the problem, which invalidate their conclusion. We shall show in the next section that physical adsorption of atoms on grains of the type proposed by Van de Hulst (1948) does not provide efficient conversion into hydrogen molecules within the age of the Galaxy. The possibility of other, more efficient, models based on chemical adsorption remains open.

2. Recombination by physical adsorption

We assume a Lennard-Jones interaction potential

$$\varphi(r) = -4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right\}, \qquad (1)$$

where ε and σ are constants, r = distance between a H-atom and any molecule of the grain surface. In view of the composition of the grains as proposed by Van de Hulst, one can estimate σ to be of the order of 3 A and ε/k, where k is Boltzmann's constant, to be between 60 and 100 °K. The latter value corresponds 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 $\varphi_{\min} = -6\varepsilon$ (Steele and Ross, 1961), Classically the adsorption energy would be equal to $|\varphi_{\min}|$. Here the first deviation from Gould and

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Salpeter's treatment occurs. According to quantum mechanics 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 $|\varphi_{\min}|$. Under the conditions mentioned above the adsorption energy of a H-atom at the grain surface is reduced from its classical value of 6ε to below 2.5 ε [see DE BOER and BLAISSE (1948), LUNBECK (1951) and ROSS and STEELE (1961)]. 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 8.7 ε. For light molecules as, for instance, H_2 and He the heat of evaporation is reduced to 2.5 ε and 0.7 ε, respectively.

We employ the following notation and values:

q_a = adsorption energy = 2.5 ε
ν_0 = vibration frequency perpendicular to surface = 10^{12} to 10^{13} sec^{-1}
T = temperature of grain = open
O = surface area of one grain = 10^{-8} cm^2
N = number density of H-atoms in cloud = 10 cm^{-3}
T_g = temperature of gas of H-atoms = 100 °K
V = average velocity of H-atoms at this temperature = 1.45×10^5 cm sec^{-1}
α = sticking coefficient = 1/3
τ = average residence time of an atom on a grain,

$$\tau = \frac{1}{\nu_0} \exp\left(\frac{q_a}{kT}\right). \qquad (2)$$

The values chosen can be justified in the following way.

(a) The sticking coefficient is experimentally found to be between 0.1 and 1 (HUNT, TAYLOR and OMOHUNDRO, 1962; BRACKMAN and FITE, 1961).

(b) The gas density is that often adopted for an average cloud. The average density near the galactic plane is much smaller; about 0.5 cm^{-3}. 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 one parsec in 10^9 years, so that it is released from the cloud only if the cloud itself expands or dissolves, which may occur in, say, 10^7 or 10^8 years. Hence it seems appropriate to maintain the high-density estimate during the entire time considered.

(c) The gas temperature is chosen between the usually adopted 130 °K and the lower values which may occur in dense clouds.

(d) 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 (VAN DE HULST, 1948; MCCREA and MCNALLY, 1960) gives at most a correction by a factor of two in the conversion rate.

(e) 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 a H-atom spends at the surface a second one arrives. This requires:

$$\tau > (\alpha\, N\, V\, O)^{-1}, \text{ or } T < T_{\max},$$

where

$$T_{\max} = \frac{q_a}{k}\left[\ln \frac{\nu_0}{\alpha N V O}\right]^{-1} = 4.5 \text{ to } 7.5\ °\mathrm{K}. \qquad (3)$$

A change in any of the quantities under the logarithm by a factor of 100 introduces a change of about 10 per cent 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

$$\frac{\alpha V N O}{\nu_0} \exp\left(\frac{q_a}{kT}\right) \approx 10^{-15} \exp\left(\frac{q_a}{kT}\right). \qquad (4)$$

For $T = 1.1\, T_{\max}$ the number of grains with two atoms is already reduced by a factor of 50 and the consequent average recombination time prolonged to 10^9 years. We may therefore conclude that at the grain temperatures usually assumed, i.e. 10 to 20 °K, the recombination mechanism based on physical adsorption of H-atoms on the grain surface is completely ineffective.

The reason for this result, which deviates from the conclusion reached by Gould and Salpeter is twofold.

(a) Gould and Salpeter did not take into account the effect of zero-point energy on q_a, which lowers q_a by a factor of about 2.5.

(b) These authors implicitly assumed that a 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.

3. Final remarks

The situation in the physical adsorption model is more favourable 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 eq. (3) we find a value for $T_{\max}$ of 10 °K for HD formation which 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 this would cause selective disappearance of atomic D with respect to atomic H and thus preferential formation of HD.

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 instance, a combination of physical and chemical adsorption might work quite well. Consider a grain with a number of sites on the surface where a H-atom is chemically more or less permanently trapped. Then the grain is virtually always occupied with H-atoms. Now a physically adsorbed atom can reach a chemically adsorbed atom by surface migration before evaporation. As Gould and Salpeter pointed out, 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.

A detailed analysis of this and other models of the grain composition is, however, outside the scope of this note.

References

J. DE BOER and B. S. BLAISSE, 1948, *Physica* **14** 149
R. T. BRACKMAN and W. L. FITE, 1961, *J. Chem. Phys.* **34** 1572
R. J. GOULD and E. E. SALPETER, 1963, *Ap. J.* **138** 393
H. C. VAN DE HULST, 1948, *Rech. Astr. Obs. Utrecht* **11** part 2
A. L. HUNT, C. E. TAYLOR and J. E. OMOHUNDRO. 1962, *Advances in Cryogenic Eng.* **8** 101
R. J. LUNBECK, 1951, Thesis, Univ. of Amsterdam
W. H. MCCREA and D. MCNALLY, 1960, *Mon. Not. Roy. Astr. Soc.* **121** 238
M. ROSS and W. A. STEELE, 1961, *J. Chem. Phys.* **35** 862
W. A. STEELE and M. ROSS, 1961, *J. Chem. Phys.* **35** 850
C. M. VARSAVSKY, 1965, Review paper at COSPAR Symp., Mar del Plata, May 1965