THE INTERSTELLAR ABUNDANCE OF THE HYDROGEN MOLECULE. I. BASIC PROCESSES*

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ABSTRACT

At present, interstellar molecular hydrogen is incapable of detection, although a high abundance has been suspected for almost two decades. In the present paper, an analysis is given of the various processes which determine the molecular concentration in H I clouds. The most important mechanism for forming molecular hydrogen is association on the surface of the interstellar grains, the characteristic time for conversion to molecular form being about 10⁸ years. It is shown that the range of grain temperatures where this recombination reaction is efficient is coincident with the range 5°-20° K, which is expected to result from the interaction with the interstellar radiation field. It is estimated that the efficiency (recombination coefficient) of the process is between 0.1 and 1. Regarding dissociative processes, photodissociation through the forbidden transition between the two Heitler-London states of the molecule, previously thought to be most important, is shown to be negligible. Ionization and dissociation of a cloud by random encounters with O and B stars occurs about once every 10⁸ years, so that if the grain recombination process is operative, a balance results in which the molecular abundance is roughly comparable with the observed atomic concentration. The cooling properties of molecular hydrogen are discussed.

I. INTRODUCTION

Radio observations of our Galaxy have shown that there are vast regions, generally taken to correspond to spiral arms, containing neutral atomic hydrogen at an average density of about 1 atom/cm³. There is, moreover, strong evidence that the hydrogen is distributed in dense "clouds" in which the density is approximately ten times as great, the clouds filling roughly 10 per cent of the interstellar space and having radii of about 5 pc. Both theory and observations point to a kinetic temperature for these socalled HI clouds that is in the neighborhood of 100° K. At this temperature, hydrogen gas, even at the low density of 10 cm⁻³, would be almost completely molecular if thermal equilibrium existed. However, the conditions in HI clouds are very far from thermal equilibrium, and a gas initially purely atomic is converted very slowly into molecular form. We shall see, however, that the most efficient mechanism for forming H_2 association on the surface of the interstellar grains-has a characteristic time possibly as short as 10⁸ years, which is two orders of magnitude less than the age of the galaxy. Thus known physical processes can produce a high molecular abundance, and this has been realized for about 15 years. Other interstellar molecules were considered at a much earlier date (cf. Swings 1938). Unfortunately, molecular hydrogen is extremely difficult to detect spectroscopically. The first bound excited electronic state of the molecule lies about 11 ev above the ground state, so that its electronic absorption lines occur well into the inaccessible ultraviolet. Being homonuclear, the molecule has no permanent dipole moment, so that its pure vibration-rotation absorption is very weak and incapable of detection. Moreover, the molecule has no fine structure or hyperfine structure splitting in the ground state, so that there can be no detection by radio emission analogous to that of the 21-cm line of atomic hydrogen. This is, of course, also the case with atomic helium, whose electronic structure is very similar to the hydrogen molecule. At present, then, there is no way of detecting interstellar molecular hydrogen. The Princeton Observatory's spectroscope-carrying satellite, which will be capable of detecting the ultra-

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violet absorption lines of interstellar H_2 , is not scheduled to be launched until 1966. A method of detecting the near infrared vibration-rotation radiation from H_2 near hot stars has been suggested by Gould and Harwit (1963) and may be applied within the next year.

The present paper constitutes an analysis of the basic physical processes which determine the molecular abundance. In calculating the various rate constants, a temperature of 100° K will be taken for the H I clouds. This is the temperature usually assumed for these regions and is the value initially given by the 21-cm investigators. If the molecular abundance is high, the cloud temperature is likely to be closer to 50° K, since the hydrogen molecule is an effective cooling agent (through radiative de-excitation of rotational levels). The latest 21-cm investigations (Clark, Radhakrishnan, and Wilson 1962) actually do point to a lower temperature, and this might be taken as weak evidence for a high molecular abundance. The rate constants calculated in this paper (except for cooling rates discussed in Sec. V) are, however, not strongly dependent (usually $\propto T^{1/2}$) on the temperature and the rough figure 100° K will be sufficiently accurate.

In Section II the various processes which form molecular hydrogen under interstellar conditions will be discussed. The most important mechanism—association on the surface of the interstellar grains—can form molecular hydrogen at a much faster (by a factor $\geq 10^{5}$) rate than other known associative processes. The physical properties of the grains are such that surface recombination should proceed efficiently. Section III is concerned with the possible dissociative processes. The principal mechanism for dissociation consists in the ionization and dissociation of the gas clouds, which results when the clouds, in their random motion, pass near bright stars. After summarizing the important processes in Section IV, the cooling properties of H₂ are discussed in Section V. Molecular hydrogen is a very effective cooling agent for an H I cloud, especially if the temperature of the cloud is above about 100° K.

In the second paper of this series (hereafter referred to as "Paper II") we shall attempt to estimate the over-all abundance and distribution of molecular hydrogen in the galaxy. The various astrophysical implications of a high molecular abundance will also be discussed.

II. MECHANISMS FOR THE FORMATION OF MOLECULAR HYDROGEN

The direct radiative association of two hydrogen atoms $(H + H \rightarrow H_2 + \gamma, \gamma \text{ denot-}$ ing the photon) is a very improbable process, especially at low temperatures. The main reason for the small recombination cross-section for two H atoms in the ground state is that the photon emitted must result from the *forbidden* transition between the two *Heitler-London* states (see Sec. III, a) of the molecule. The radiative recombination of one H atom in the ground state and the other in, say, the 2p excited state proceeds through an allowed transition, but the fraction of H atoms in the 2p or in other excited states is so small that such processes can be neglected. Because of the failure of this basic recombination process, it is necessary to consider other more indirect mechanisms for the formation of molecular hydrogen. We shall, in particular, consider certain catalytic processes, since hydrogen is the most abundant element of the interstellar gas and only catalytic or cyclic processes are capable of converting large amounts of hydrogen to molecular form. The most efficient such catalytic process is the recombination reaction on the surface of the interstellar grains, first suggested as a mechanism for forming interstellar H₂ by van de Hulst. In this process the excess energy resulting from the formation of a stable molecule is transferred into lattice vibrations of the grain.

a) Association on Interstellar Grains-Basic Ideas

The simplest assumption that one can make regarding this recombination reaction is that every hydrogen atom that hits the grain surface eventually leaves as one of the constituents of a hydrogen molecule. By making this assumption, one can calculate the

rate of molecule formation from a knowledge of the hydrogen atom density and the amount of grain surface area per cm³ of interstellar space. Thus the number of molecules formed per cm³ per second would be

$$\dot{n}_{\rm H_2} = \frac{1}{2} J A$$
, and $J = \frac{1}{4} n_{\rm H} \bar{v}$, (1)

where J is the flux of hydrogen atoms from the surrounding gas, \bar{v} is the mean thermal velocity of the atoms, and A is the amount of grain surface area per cm³. The quantity A can be estimated from the data on interstellar extinction. McCrea and McNally (1960) have done this for spherical grains of density 1.1 gm/cm³, and their results may be expressed in terms of the "smeared-out" grain density ρ_{gr} inside one cloud as

$$\dot{n}_{\rm H_2} = \gamma b n_{\rm H} \rho_{\rm gr} \,. \tag{2}$$

In equation (2) a factor γ , called the *recombination coefficient*, has been introduced and represents the *fraction* of atoms striking the grain surface that eventually leave as part of a molecule; *b* is a constant which depends on the velocity \bar{v} of the H atoms and the ratio of average surface area to mass of the grains. The results of McCrea and McNally give $b \simeq 4.1 \times 10^9$ cm³/gm-sec. For a typical cloud in which $n_H = 10$ cm⁻³ and $\rho_{gr} = 10^{-25}$ gm/cm³, the formation rate would be

$$\gamma_g \equiv 2\dot{n}_{\rm H_2}/n_{\rm H} \simeq \gamma \times 8 \times 10^{-16} \, {\rm sec}^{-1} \,, \tag{3}$$

giving a characteristic formation time $\sim \gamma^{-1} \times 4 \times 10^7$ years.

The value of the recombination coefficient γ is clearly of prime importance, and in the literature there have appeared a number of suggestions as to its appropriate magnitude. The references to experimental work on surface recombination done at room temperature are completely irrelevant, however. For the interstellar grains are likely to be very cold ($T \approx 5^{\circ}-20^{\circ}$ K) and atoms and molecules are likely to be adsorbed by the weak van der Waals forces, which are not strong enough to bind atoms to the surface of a solid at room temperature. The mechanism for recombination at low temperature is thus quite different from that at high temperatures, where the recombination occurs through the relatively strong interactions of valence forces. In this section we shall attempt to determine the range of grain temperatures where the recombination coefficient γ is close to unity. This can be done quite easily because essentially all that one has to know is the binding or adsorption energies of hydrogen atoms and molecules to the surface of the grain. The adsorption energy can be easily calculated in terms of the characteristic parameters of the van der Waals forces between the adsorbed atom or molecule and the atoms of the grain.

For convenience, we take the surface of the grains to be an ideal one (effects of irregularities will be discussed later). In the steady state the fraction (θ) of the surface that is covered with adsorbed hydrogen *atoms* will be determined by an equation of the form

$$J(1-\theta) = u_e\theta + 2u_r\theta^2, \qquad (4)$$

where J is defined in equation (1) and u_e and u_r will be discussed below. The term on the left-hand side of this equation corresponds to a replenishment of the unoccupied surface equilibrium sites; the first term on the right corresponds to thermal evaporation of atoms from the surface; the second term on the right denotes the removal of atoms from the surface by recombination. It is assumed that the molecule formed on the surface of the grain eventually escapes into the interstellar gas. Actually, this imposes a condition on the temperature of the grain, as will be discussed later. The significance of the term $J(1 - \theta)$ in equation (4) is clear; $J(\sim 3 \times 10^5 \text{ cm}^{-2} \text{ sec}^{-1})$ is just the flux of atoms from the surrounding gas which hit the surface of the grain. It is assumed that each atom that hits the surface sticks to it. Van de Hulst (1949) has quoted experimental

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work suggesting that this is a reasonable assumption. The evaporation rate constant u_e would be given by (approximately)

$$u_e = \nu_0 \sigma_0 e^{-q_a/kT} , \qquad (5)$$

where $\nu_0(\sim 10^{13} \text{ sec}^{-1})$ is the characteristic frequency for vibration perpendicular to the surface; $\sigma_0(\sim 10^{15} \text{ cm}^{-2})$ is the number of equilibrium (minimum energy) sites per cm² of surface, and the exponential factor represents essentially the probability of being evaporated per vibration, q_a being the adsorption energy and T the grain temperature. The recombination term $2u_r\theta^2$ represents the effect of molecule formation in the adsorbed layer. Now, at low interstellar densities, the rate J of atoms hitting the surface is small (characteristic time for filling an occupied site: $\sigma_0/J \sim 100$ years). Atoms hitting the surface have plenty of time to wander about on the surface of the solid, and this migration may be considered equivalent to the motions of a two-dimensional gas whose particles move with a velocity $v_2 \sim v_0' a D_0$, v_0' being the frequency of vibration in the surface, and D_0 a diffusion factor. If the surface migration were due to thermal motions, D_0 would be given by

$$D_0^{(\text{th})} \sim e^{-E_b/kT}$$
, (6)

where E_b is the energy barrier between adjacent sites. For the very low temperatures that the grains have, there is a more efficient migration mechanism: the energy barrier E_b may be surmounted by quantum-mechanical tunneling. In this case the diffusion factor D_0 would be given by

$$D_0^{(q.m)} \sim \langle e^{-t} \rangle$$
, (7)

where $\langle e^{-t} \rangle$ is an appropriate quantum-mechanical average over the one-dimensional WKB barrier penetration factor (Landau and Lifshitz 1958), in which

$$t = \frac{2}{\hbar} \int_{a}^{a'} | p | dx.$$
⁽⁸⁾

In relation (8), a and a' represent the two classical turning points of the barrier. The energy barrier depends on the height of the atom above the surface of the solid. The quantum-mechanical average in equation (7) is then clearly

$$D_{0} = \langle e^{-t} \rangle = \langle v \mid e^{-t(h)} \mid v \rangle$$

= $\int dh \psi_{v}^{2}(h) \exp \left[\frac{2}{\hbar} \int |p(x;h)| dx\right],$
⁽⁹⁾

where $\psi_v(h)$ is the normalized wave function for vibrational motion perpendicular to the surface of the solid. For the small energies involved in van der Waals binding, the diffusion factor calculated from equation (9) turns out to be surprisingly large. A value $D_0 \sim 10^{-2}$ was calculated for the expected binding energies (see part *b* of this section) and a spacing between equilibrium sites of 3 A. The quantum-mechanical diffusion constant is, of course, independent of temperature. If a pair of adsorbed hydrogen atoms happen to come within about two lattice spacings ($\sim \sigma_0^{-1/2}$) and if their electron spins are such that they form a singlet state (relative probability: $\frac{1}{4}$), they will be attracted by the strong tail of the potential of the ${}^{1}\Sigma_{\sigma}$ (ground) state of H₂. The two atoms will then form the bound system H₂, with the recombination energy being transmitted into the crystal lattice. Hence, with our two-dimensional gas picture for the recombination process the atoms move about with a velocity $\sim \nu_0' \sigma_0^{-1/2} D_0$; when they come within

about $\sigma_0^{-1/2}$ (the one-dimensional "cross-section"), there is a recombination. Since the number of occupied sites per unit area is $\sigma_0 \theta$, we have

$$2u_r \sim \nu_0' \sigma_0 D_0 \sim 10^{26} \text{ cm}^{-2} \text{ sec}^{-1}$$
 (10)

Thus, independently of grain temperature $u_r \gg J$.

When the grains are cool enough that evaporation (the term $u_e\theta$ in eq. [4]) is negligible, θ is approximately given by

$$\theta = \left(\frac{J}{2u_r}\right)^{1/2} \ll 1 , \qquad (11)$$

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and the recombination coefficient by (eq. [3])

$$\gamma = \frac{2u_r\theta^2}{J} \simeq 1 - \left(\frac{J}{2u_r}\right)^{1/2} \left(1 + \frac{u_e}{J}\right). \tag{12}$$

We see from equation (11) that if the recombination coefficient is to be close to unity, we must have

$$\left(\frac{J}{2u_r}\right)^{1/2} \left(1 + \frac{u_e}{J}\right) \ll 1.$$
⁽¹³⁾

The only way in which this inequality could fail to be satisfied is by the term u_e/J being very large. Substituting the expressions for the rate constants u_r and u_e , we obtain the following condition on the grain temperature $(\nu_0' \sim \nu_0)$:

$$e^{2q_a/kT} > \frac{\kappa}{D_0}, \qquad \kappa \equiv \frac{\nu_0 \sigma_0}{J}, \tag{14}$$

the right-hand side of the inequality (14) being very large ($\sim 10^{24}$). The meaning of result (14) is the following: if the grain temperature is greater than a maximum value given by

$$T_m = \frac{k}{2q_a} \ln\left(\frac{\kappa}{D_0}\right),\tag{15}$$

the hydrogen atoms which are captured by the grain will be evaporated before they have a chance to recombine and form H_2 .

There is an additional condition on the grain temperature. It has been assumed that the molecules formed on the grain are eventually ejected from the surface. A number of authors have argued that, since about 4.5 ev of energy are released in recombination, the molecule can easily break loose from the surface to which it is initially bound by a much smaller potential. This is not necessarily true. For the 4.5 ev is *vibrational* energy, and, for the molecule to escape from the surface, this energy must be transferred to translational motion away from the surface. The vibrational interchange is not efficient, since the energy must be transferred in essentially one vibration period of the molecule an unlikely process, considering the strength of the interaction with the solid. If the molecules cannot be ejected immediately on formation, they must be ejected by thermal means. Thus the thermal evaporation of *molecules* must keep up with the replenishment of the surface by atoms from the gas; otherwise, a monolayer of molecular hydrogen will build up on the surface. This requirement leads to a second condition on the grain temperature:

$$e^{q}m^{/kT} > \kappa , \qquad (16)$$

where q_m is the adsorption energy of the hydrogen molecule. Actually, a condition of type (16) would result even if the hydrogen molecules were ejected immediately on

recombination. For then a monolayer of H₂ would form on the surface as a result of the impinging hydrogen *molecules* from the surrounding gas. The parameter $\kappa [\alpha (\text{density})^{-1}]$ would then be calculated from the density n_{H_2} of molecules. Since $\kappa (\sim 10^{22})$ is very large, the resulting critical temperature,

$$T_c = \frac{k}{q_m} \ln \kappa , \qquad (17)$$

will not vary appreciably unless the molecular density is many orders of magnitude less than the atomic density. For this reason, we shall calculate T_c using the atomic density in κ .

We see that if the recombination coefficient is to be close to unity, the grain temperature must be within the limits

$$T_c < T < T_m,$$

with T_c and T_m given by relations (15) and (17). Above T_m the adsorbed atoms evaporate before they have a chance to form molecules. Below T_c a monolayer of H₂ forms on the surface of the grain, thus changing its catalytic properties. Actually, if such a monolayer exists, recombination can still take place if the grain temperature is within a second set of limits. Recombination can occur on the H_2 monolayer if the grain temperature is low enough that hydrogen atoms adsorbed above the monolayer do not evaporate before recombining. The temperature has to be high enough, however, that a second layer does not form. Thus, if the grains are cool enough, there is a second range of temperature $T_c' < T < T_{m'}$, where $\gamma \to 1$. The quantities T_c' and $T_{m'}$ are defined in analogy with equations (15) and (17), but their numerical values are different, since the corresponding adsorption energies q_a' and q_m' are lower. There are no other regions at even lower temperatures corresponding to double (and triple, etc.) layers where recombination occurs, since such multilayers would approximate solid H₂, which can exist only below about 2.5° K under interstellar conditions. All estimates of grain temperatures give values higher than this. The temperature ranges where $\gamma \rightarrow 1$ are determined essentially by the adsorption energies and the calculation of these quantities is outlined in part b of this section.

b) Adsorption Energies—Temperature Dependence of the Recombination Coefficient

To calculate the adsorption energies of hydrogen atoms and molecules to the surface of the interstellar grains, one must know the chemical nature of the grains. Van de Hulst (1949) has suggested the following relative composition for the grains: 100, 30, 20, 10, and 5 molecules, respectively, for H₂O, H₂, CH₄, NH₃, and MgH plus other species. As a solid, the grains would be classified somewhere between a hydrogen-bonded crystal (ice) and a molecular crystal. To estimate adsorption energies, we shall take an idealized model for the grains. We assume a body-centered cubic lattice with identical force centers at the lattice points x_i , y_i , $z_i = ip_i(i + \frac{1}{2})p$ (i = 0, 1, 2, 3, ...), p being the lattice constant. The density of force centers is then $n = 2p^{-3}$. For the interaction between the adsorbed atom and these force centers, we take a 6-12 type of potential:

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right].$$
(18)

The function (18) is characterized by only two parameters, the strength parameter ϵ and the range parameter σ ; it has a minimum value $-\epsilon$ at $r = 2^{1/6}\sigma$. For most interacting systems (for example, H-H₂ and H₂-H₂), $\sigma \approx 3$ A. From considerations of the density of ice, a value $p \approx 3$ A seems appropriate, and in the calculation of adsorption energies it will be assumed that $\sigma = p$. To calculate the magnitude of the adsorption energy,

it is necessary to calculate the potential curve $\varphi(h)$, where h is the height above the top layer of the solid; $\varphi(h)$ is given by

$$\varphi(h) = \sum_{i} \varphi(r_{i}), \qquad (19)$$

the sum being over the lattice sites. For reasons of symmetry, the *minimum* values of $\varphi(h)$ can occur above only three positions in the plane of the top layer of "atoms" (or force centers) of the solid: (A) above the mid-point of four surface atoms, (B) above a surface atom, or (C) above the mid-point of two surface atoms. Performing the summation over lattice sites and calculating the potential curves, one finds that case A gives the lowest energy, the value being $\varphi_{\min}/4\epsilon \simeq -1.5$. Case C gives the next lowest energy, and this determines the "easiest" path for migration between adjacent equilibrium sites,



FIG. 1.—Recombination coefficient as a function of grain temperature for various values of ϵ_0

that is, the "saddle" is above the mid-point of two surface atoms. One can also calculate the potential curves for, say, a hydrogen atom above the solid which has a monolayer of H₂; but here two strength parameters are involved, one for the H-H₂ interaction, the other for the interaction H-X between the hydrogen atom and the force centers of the bare solid. Now the potential curve for the H-H₂ system has been calculated by Margenau, the curve being reproduced in the book of Hirschfelder, Curtis, and Bird (1954). For this system, ϵ averaged over relative orientations of the molecule is about 4.0 \times 10^{-15} erg, and this will be taken later as the fundamental energy unit. The experimental value of ϵ for the H₂-H₂ system is 5.0 \times 10⁻¹⁵ erg, and we shall assume that the interaction parameters of hydrogen atoms and hydrogen molecules with the force centers (X)of the solid are related by $\epsilon_{H-X}/\epsilon_{H_2-X} = \frac{4}{5}$. With this assumption, one can calculate all the pertinent adsorption energies and thus the temperature variation of the recombination coefficient by specifying the interaction parameter $\epsilon_{H-X} \equiv \epsilon_0$. The results of these calculations are shown in Figure 1 for several values of ϵ_0 . We see that there are two temperature ranges where $\gamma \rightarrow 1$; there is one at higher grain temperatures where the recombination occurs on the bare surface, and there is a narrower range at lower temperatures where recombination occurs on top of the H_2 monolayer. Now the strength

parameter of the 6-12 potential is roughly proportional to the product of the electronic polarizabilities of the interacting species. The polarizabilities of the molecules suspected of being the chief constituents of the grains are about two or three times as large as the polarizability of the hydrogen molecule. One would expect, then, that the appropriate value of ϵ_0 would be (roughly) between 2ϵ and 3ϵ . It is significant that the resulting maxima in the curves in Figure 1 occur within the expected range 5°-20° K of the grain temperature.

The calculated results are, of course, for an idealized solid, and the surface of the grains is probably quite irregular. These irregularities would tend to smear out the region where $\gamma \rightarrow 1$. Moreover, since the grains are expected to have a distribution of sizes, there will also be a distribution of grain temperatures. Because of these effects, the mean value of the recombination coefficient is likely to be somewhere between 0.1 and 1, so that the physical characteristics of the grains seem to be quite favorable for molecule formation.

It should be noted that our theoretical estimate for γ for a grain with a regular surface at a given temperature could be in error by very many orders of magnitude in either direction, because of the very large Boltzmann factors involved in the various expressions. For the same reason, however, it seems likely that γ for a regular surface would be exceedingly close to unity in *some* ranges of temperature and that our estimates for the relevant temperatures are not likely to be in error by factors of more than 2 or so. Paradoxically, it is thus the complexity of the irregular grain surfaces and the distribution of grain temperatures that give us some confidence (but no guaranty) that the *average* value of γ is not much smaller than unity.

There has been some recent experimental work which shows that solid surfaces at very low temperatures can be very efficient in the catalytic formation of molecular hydrogen. Brackmann and Fite (1961) directed a thermal ($T \approx 80^{\circ}$ K) beam of partially dissociated hydrogen at a cooled copper surface and measured the reflection probability of the atomic hydrogen as the temperature of the solid surface was lowered from 80° to 3° K. They found that recombination occurred very efficiently when the temperature of the solid surface was between 10° and 20° K. According to Brackmann and Fite, their surface probably consisted of frozen air at these temperatures.

According to equations (2) and (3), molecule formation leads to an exponential decrease of the atomic hydrogen concentration with time if the grain density ρ_g and the *total* hydrogen density n_0 ($= n_{\rm H} + 2n_{\rm H_2}$) remain constant during the molecular conversion. If initially the molecular concentration in a cloud is zero, the *fraction* of the hydrogen in molecular form at a later time t is given by

$$F(t) = 1 - e^{-\gamma_g t}, \qquad \gamma_g = 2\gamma b\rho_g \simeq \gamma \times 8 \times 10^{-16} \text{ sec}^{-1}, \tag{20}$$

the probable value of γ being between 0.1 and 1. Recombination times are thus of the order of 10⁸ years, and this is the main result of Section II. It should be pointed out here that if the number of very small grains, which do not contribute to optical absorption and for which, therefore, there are no data regarding their abundance, should turn out to be very large and contribute more than optical size grains, the recombination time could be shortened considerably. On the other hand, if the grains should turn out to have physical properties vastly different from what is presently thought, the surface recombination process could be inoperative.

c) Alternate Mechanisms for Forming Molecular Hydrogen

Here we consider a number of other mechanisms for molecule formation. These alternate mechanisms are only capable of producing a molecular density much smaller than that resulting from the catalytic reaction on grain surfaces. Nevertheless, the alternate mechanisms can usually be understood better than the grain recombination

reaction, and it is important to consider them, especially if the grains should turn out to be of a vastly different nature than presently thought.

Herzberg (1955) has enumerated a number of exothermic reactions of the form $AB + C \rightarrow AC + B$ which produce molecular hydrogen. The activation energies for these reactions may be estimated from the semiempirical relation $A = 0.055 D_{AB}$, D_{AB} being the dissociation energy of the molecule AB. One such reaction is

$$CH+H \rightarrow C+H_2$$
,

for which an activation energy A = 0.19 ev is estimated. The activation energy is so high that the reaction is extremely slow¹ at the normal H I cloud temperature of 100° K. However, if a cloud is heated to, say, 1000° K in a cloud-cloud collision, the reaction proceeds very rapidly, and, in fact, all the CH in the cloud would be converted by means of this reaction. The CH concentration in H I clouds is known to be about $n_{\rm CH} \sim 10^{-7}$ cm⁻³, while the cloud-cloud collision frequency is about $Z \sim 10^{-14}$ sec⁻¹. The rate of formation of H₂ in a typical cloud by this process would then be $Zn_{\rm CH} \sim 10^{-21}$ cm⁻³ sec⁻¹, which is about six orders of magnitude smaller than the rate of formation on the interstellar grains.

Reactions involving the molecular ion H_2^+ —for example, the radiative capture process $H_2^+ + e \rightarrow H_2 \gamma$ —may also be shown to be quite negligible. The molecular ion is difficult to form by radiative association $(H + p \rightarrow H_2^+ + \gamma)$ at low temperatures. Moreover, even if the molecular ion does form, it will very quickly undergo *dissociative recombination* $(H_2^+ + e \rightarrow 2H)$; only a small fraction $(\sim 10^{-5})$ of the electron captures leads to the products $H_2 + \gamma$.

The reaction

$$\mathrm{H}^- + \mathrm{H} \rightarrow \mathrm{H}_2 + e$$
,

called *associative detachment*, has been considered recently by McDowell (1961) as a mechanism for producing molecular hydrogen in H I clouds. The rate of formation of H_2 by this mechanism would be given by

$$\dot{n}_{\rm H_2} = a_{\rm ad} n_{\rm H} n_{\rm H^-} , \qquad (21)$$

where a_{ad} is the rate constant. The H⁻ concentration is determined by photodetachment $(\gamma + H^- \rightarrow H + e, \text{ rate constant: } \gamma_p)$ by the galactic radiation field and the reverse reaction, radiative association (rate constant: a_{ra}), and is given by

$$n_{\rm H^-} = \frac{\alpha_{\rm ra}}{\gamma_p} n_{\rm H} n_e \,. \tag{22}$$

Substituting this expression into equation (20), we have, for the rate of formation of molecular hydrogen by this process,

$$\dot{n}_{\rm H2} = \frac{a_{\rm ad} a_{\rm ra}}{\gamma_p} n_{\rm H}^2 n_e.$$
⁽²³⁾

McDowell estimates for the rate constants: $a_{ad} = 1.2 \times 10^{-11} T^{1/2} \text{ cm}^3 \text{ sec}^{-1}$; $a_{ra} = 1.5 \times 10^{-17} T^{1/2} \text{cm}^3 \text{ sec}^{-1}$, where T is the kinetic temperature; and $\gamma_p = 2 \times 10^{-7} \text{ sec}^{-1}$, the last value carrying the greatest uncertainty. If we take the usual cloud densities $n_{\rm H} = 10 \text{ cm}^{-3}$ and $n_e = 2 \times 10^{-3} \text{ cm}^{-3}$ and a temperature of 100° K, we calculate a rate $\dot{n}_{\rm H_2} = 2 \times 10^{-20} \text{ cm}^{-3} \text{ sec}^{-1}$ from equation (23).

¹ Even if the activation energy were zero, the rate of formation of H_2 by this process would be several orders of magnitude less than the rate of formation on the interstellar grains. Actually, if A were zero, essentially all the CH in a typical cloud would be transformed by the chemical-exchange process in about 100 years, and it would be difficult to explain the observed presence of the molecule CH without an efficient process for forming it.

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The reaction involving the negative hydrogen ion is quite well understood. There is no doubt that H⁻ exists in the interstellar clouds, for there are certain to be free electrons around, which can attach themselves to hydrogen atoms. Even if the carbon atoms, which are thought to provide (by photoionization) the free-electron density, are locked up in the interstellar grains, roughly the same electron density would result from ionization of hydrogen atoms by the lower limit to the cosmic-ray flux. The associative detachment process will thus provide a firm lower limit for the expected concentration of interstellar molecular hydrogen. This lower limit is, however, about five orders of magnitude smaller than the concentration expected from the catalytic formation on the surface of the interstellar grains.

III. DISSOCIATIVE PROCESSES

In this section the various processes will be discussed that tend to limit the amount of molecular hydrogen produced in the galaxy. It will be shown in part *a* that the importance of the photodissociative transition between the two *Heitler-London* states of the molecule, previously thought to be the principal mechanism for dissociation, has been overestimated and that the mechanism is, in fact, of negligible importance. In part *b* a brief account of the effects of cloud-cloud collisions is given. The following subsection (*c*) gives a short discussion of the problem of determining the mean rate of ionization of the clouds by random passage near O and B stars. This process appears to be the most important mechanism for dissociating interstellar H_2 and is treated in some detail in Paper II. The last part of this section (*d*) is devoted to a discussion of the dissociative effects of cosmic rays.

a) Photodissociation through the Forbidden Transition

The threshold for photodissociation of H_2 through an allowed transition is at 14.5 ev, corresponding to a dissociation in which one of the hydrogen atoms is left in the n = 2 state. Photoionization occurs beyond an even higher threshold of 15.4 ev. Because of the high opacity of atomic hydrogen for photon energies greater than 13.6 ev (with a density $n_{\rm H} = 10$ cm⁻³ and a path length of 1 pc, the optical thickness at the Lyman limit is about 20), the general galactic radiation field suffers a cutoff inside the cloud, and no photons sufficiently energetic to easily photodissociate or photoionize H_2 are available.² This situation led Kahn (1955*a*) to consider a dissociative process involving photons of lower energy.

At the equilibrium internuclear separation for the ground state, the energy difference between the two Heitler-London states ${}^{1}\Sigma_{g}$ (the ground state) and ${}^{3}\Sigma_{u}$ (the repulsive state) of H₂ amounts to about 8-10 ev. A transition between these two states could be induced by photons from the galactic radiation field and would result in a dissociation of the molecule. However, the transition is forbidden by the selection rule $\Delta S = 0$ and has a very small oscillator strength or *f*-value. The oscillator strength is proportional to the matrix element of the dipole operator between the two states, and if the ground state were purely singlet and the upper state purely triplet, this matrix element would vanish identically because of the orthogonality of the spin eigenfunctions. Because of spin-orbit and spin-spin interactions, the ground state ${}^{1}\Sigma_{\sigma}$ has a small triplet component of relative amplitude $\sim H'/\Delta E$, where H' is of the order of the spin-orbit or spin-spin interaction energy and ΔE is of the order of the characteristic electronic energies. Hence $H'/\Delta E \sim a^2$, where $a(\approx 1/137)$ is the fine structure constant. Similarly, the ${}^3\Sigma_u$ state has a singlet component of amplitude $\sim a^2$. Since the *f*-value is proportional to the square of the dipole matrix element, the oscillator strength is proportional to the square of the amount of singlet-triplet mixing or to a^4 . Thus we can expect an oscillator strength which is down from ordinary strong allowed dipole transition f-values (~ 1) by $\sim a^4$. A reason-

² We discuss in Sec. III the radically different conditions which arise when the cloud happens to be near an O or B star.

able estimate for the oscillator strength is³ 10^{-8} – 10^{-10} . Adopting a value 10^{-9} , one calculates, using the estimated value of the interstellar radiation field (Lambrecht 1955), a dissociation rate constant $3 \times 10^{-18} \text{ sec}^{-1}$. This rate constant is four orders of magnitude smaller than the value calculated by Kahn (1955*a*), the discrepancy being due to the large value 10^{-5} used by Kahn for the oscillator strength. The process is essentially of negligible importance, since, as will be shown, there are other mechanisms for dissociation of H₂ that have larger rate constants.

b) Cloud-Cloud Collisions

As will be discussed in more detail in Paper II, the gas clouds have random motions characterized by a mean velocity \bar{v} of about 15 km/sec. Because of these random motions, the clouds can undergo inelastic collisions (frequency: $Z \sim 10^{-14} \text{ sec}^{-1}$) in which the kinetic temperature of the clouds is raised to a few thousand degrees Kelvin (Kahn 1955b). After a collision the cloud is quickly cooled (especially if the molecular abundance is high, since H₂ radiates away energy efficiently), so that the high temperature lasts only a short time and very little of the molecular hydrogen is dissociated. Of course, if magnetic fields prevent the clouds from penetrating and make the collision nearly elastic, the heating of the clouds will be reduced. In any case, while there is very likely to be some heating of the clouds in collisions, the probability of transferring 4.5 ev ($\approx 52000^{\circ}$ K/k) to the molecule in order to dissociate it is quite small for most cloud-cloud collisions. A much more important dissociative effect of cloud motions consists in the ionization of the clouds by random passage near O and B stars. The ionization effects are discussed briefly in the next section.

c) Ionization of H I Clouds by O and B Stars

When a cloud passes near a bright star, it becomes dissociated and ionized as the ultraviolet radiation rapidly eats its way through the cloud. Dissociation of H₂ occurs either (i) by direct photodissociation (threshold: 14.5 ev) through allowed transitions in which one of the hydrogen atoms goes off in the first excited state or (ii) photoionization (threshold: 15.4 ev) in which the molecular ion H₂⁺ is then quickly dissociated through either dissociative recombination (H₂⁺ + $e \rightarrow 2H$) or photodissociation ($\gamma + H_2^+ \rightarrow H + p$). Dissociative recombination is very rapid⁴ since the process does not involve the emission of a photon and thus the cross-section does not have powers of the fine-structure constant as a factor. By means of these processes, a cloud (or at least a certain fraction of it) becomes completely ionized when it is in the vicinity of a bright star. If it is not completely disrupted on ionization, the cloud will quickly be neutralized by electron-proton radiative recombination when it moves away from the star. Molecule formation will then take place at a much slower rate.

The general phenomenon of the ionization of H_{I} clouds will be discussed in detail in the second paper of this series, where the dynamical motion of clouds throughout the galactic disk is considered. The result is essentially the following. The effective rate constant for ionization is given by

$$\gamma_i = \bar{v} \langle \lambda_i^{-1} \rangle , \qquad (24)$$

where \bar{v} is the mean cloud velocity and $\langle \lambda_i^{-1} \rangle$ is the reciprocal of the mean free path for cloud ionization averaged over all values of z, the height above the plane of the galaxy. The weight factor used to calculate $\langle \lambda_i^{-1} \rangle$ is essentially the observed spatial distribution

³ In a recent unpublished investigation G. Herzberg and H. C. Longuet-Higgins have independently arrived at essentially the same result (G. Herzberg, private communication).

⁴ Unfortunately, there is conflicting experimental evidence concerning this point (Biondi and Brown 1949; Persson and Brown 1955). However, it is not crucial to our arguments whether dissociative recombination occurs efficiently or not.

in the z-direction of atomic hydrogen. In the plane (z = 0) of the galaxy, λ_i is calculated to be roughly 1 kpc, while the harmonic means is about twice as large, giving an effective rate constant $\gamma_i \sim 3 \times 10^{-16} \text{ sec}^{-1}$. Thus the clouds are ionized about once every 10^8 years.

The process of ionization (and dissociation) by O and B stars appears to be the most important mechanism for limiting the amount of molecular hydrogen formed in H I clouds. Since the time scales for formation and dissociation are roughly the same, a steady-state condition results in which the molecular abundance is comparable with the observed atomic concentration.

d) Cosmic Rays and Suprathermal Particles

Cosmic-ray protons cause ionization (formation of H_2^+) of hydrogen molecules. Since the resulting molecular ion is quickly dissociated, either by photodissociation or by dissociative recombination, formation of H_2^+ can be considered equivalent to breaking up the molecule. Most of the data available on the cosmic-ray flux is for energies greater than 10 Bev, where the flux follows a power-law spectrum (Singer 1958)

$$j(E) = \frac{dJ}{dE} = 0.46E^{-2} \text{ 15 protons/cm}^2/\text{sec/ster/Bev interval}, \qquad (25)$$

where $E = T + Mc^2$ is the *total* energy in Bev. At these high energies the cross-section for ionization of a hydrogen atom or molecule is very small, and the ionization rate is negligible. Magnetic fields in the solar system prevent the observation of the low-energy part of the cosmic-ray energy spectrum, so that considerations of the flux in this region must involve unverified theory. Unfortunately, the low-energy cosmic rays are most important here because the cross-section for ionization increases at low energy. A Fermi I type mechanism (Fermi 1949) for the acceleration of cosmic rays, which requires an *injection* energy of about 100 Mev, produces a rate constant for ionization of about 5×10^{-19} sec⁻¹ when the predicted low-energy spectrum is fitted to the high-energy data. This rate constant is quite small, but its numerical value is based on the Fermi theory, which is of doubtful validity.

Hayakawa, Nishimura, and Takayanagi (1961) favor the existence of so-called "suprathermal" particles, whose energy spectrum extends below the injection energy for the Fermi mechanism. These particles are supposed to have a much larger low-energy flux than the ordinary cosmic-ray protons, and, in fact, Hayakawa *et al.* take a j(E) spectrum with a peak at 10 Mev. There is, of course, no observational evidence for the existence of these suprathermal particles and no accepted theory of their origin. The hypothesis was first introduced to explain the observed temperature of H I regions by means of the heating produced by their ionization of the interstellar medium. However, as Kahn (1955b) has shown, cloud-cloud collisions can produce sufficient heating to explain the magnitude of the temperature. There thus appears to be no need for postulating the existence of suprathermal particles, since all observable phenomena can be explained by other means.

Our lack of knowledge of the low-energy cosmic-ray flux is readily admitted, however, and an upper limit to the flux is desirable. One upper limit may be obtained from considerations of the temperature of H I clouds. On the assumption that cooling is due to excitation of low-lying states of C⁺, Si⁺, and Fe⁺ ions (see Sec. V of this paper) and heating is due solely to cosmic rays (or suprathermal particles), Hayakawa *et al.* have shown that a temperature of 125° K would result in clouds of density $n_{\rm H} = 10$ cm⁻³ if the rate constant for ionization of hydrogen atoms was $\sim 10^{-15}$ sec⁻¹. The rate constant needed to produce a temperature of 60° K is, however, an order of magnitude smaller. Electronic excitation of ions is more important than excitation of rotational levels of hydrogen molecules under these conditions because of the high electron density ($\simeq 0.01$ -

 0.03 cm^{-3}), which is produced by the ionization of hydrogen atoms (and molecules) by the high cosmic-ray flux. The rate constant for ionization of H₂ by cosmic rays can be expected to be of the same order of magnitude as the rate constant for ionization of H. Hence the upper limits quoted here may also be taken to correspond to the rate of dissociation of H₂ by cosmic rays.

If gas temperatures of about 60° K should be confirmed in future experiments, giving the upper limit $\sim 10^{-16}$ sec⁻¹ for the cosmic-ray ionization rate, the effects of cloud encounters with O and B stars, for which the effective dissociation rate is $\sim 3 \times 10^{-16}$ sec⁻¹, should be considered more important. If the higher temperature of 120° K is confirmed, the upper limit $\sim 10^{-15}$ for the cosmic-ray ionization rate would not allow one to neglect their effect with great confidence. However, since there is no positive observational evidence for the large low-energy cosmic-ray flux and since it is unlikely that their actual associated ionization rate is close to the upper limit, we shall assume that they are of negligible importance.

IV. SUMMARY

Interstellar grains appear to have physical properties that make them efficient catalysts for the formation of molecular hydrogen. The recombination coefficient γ is estimated to be between 0.1 and 1. For typical H I clouds, the characteristic time for molecule formation can be as short as 10⁸ years and is not likely to exceed 10⁹ years. The associative detachment reaction H⁻ + H \rightarrow H₂ + *e* provides an alternate mechanism for formation of H₂, which, however, is slower than grain recombination by a factor $\sim 10^{-5}$.

The photodisssociation process resulting from a transition between the two *Heitler*-London states, previously thought to be the principal mechanism for dissociation, is of negligible importance because of the small oscillator strength involved. The most important dissociation mechanism appears to be the ionization of the clouds by random passage near O and B stars, the mean time between ionizations being about 10⁸ years. The physical picture as regards molecular buildup is then the following. Molecules form gradually in H I clouds by surface recombination on the interstellar grains. In its random motion throughout the galactic disk the cloud makes a chance encounter with a bright star and becomes ionized and dissociated, essentially instantaneously. The molecular concentration in individual clouds will then be different, depending on how recently the cloud was ionized. The average fraction of the hydrogen in molecular form in different parts of the galaxy will be calculated in detail in Paper II. Since the recombination time is comparable with the ionization (and dissociation) time, the analysis predicts an appreciable fraction in molecular form.

V. COOLING PROPERTIES OF MOLECULAR HYDROGEN

Molecular hydrogen is very efficient as a cooling agent for H I clouds. When the rotational levels of H₂ are excited by collisions with H atoms, the levels can be depopulated by radiation, thus allowing energy to escape from the cloud. For the expected cloud temperature $\approx 100^{\circ}$ K, most of the molecules will be in the ground rotational state (J = 0) of para-hydrogen, and the principal excitation is to the J = 2 state. As Osterbrock (1962) has emphasized, the J = 2 level is likely to be de-excited via the para-ortho-para sequence $J = 2 \rightarrow 1 \rightarrow 0$, the lifetime of the J = 2 state being $\sim 10^{9}$ seconds. Since this time is shorter than the time ($\sim 3 \times 10^{10}$ sec) for collisional de-excitation (Takayanagi and Nishimura 1960, hereafter referred to as "TN"), essentially all the excitations result in radiative transition downward, in which two photons, the sum of whose energy equals the excitation energy of the J = 2 state, escape from the cloud. The rate of energy loss per cm³ by this process would then be given by

$$\Lambda_{\rm HH_2} = n_{\rm H} n_{\rm H_2} \langle v Q_{0 \to 2} \rangle \Delta E_r , \qquad (26)$$

where $\langle vQ_{0\to 2} \rangle$ is the product of the relative velocity of the hydrogen atom and molecule and the excitation cross-section averaged over the relative velocity distribution and $\Delta E_r (=0.044 \text{ ev} = k \times 510^{\circ} \text{ K})$ is the excitation energy of the J = 2 state. The quantity $\langle vQ_{0\to 2} \rangle$ has been calculated by TN for various temperatures. The cross-sections Q for such excitations of hydrogen molecules by hydrogen atoms are much larger than the crosssections for excitation by molecule-molecule collisions. It is for this reason that a corresponding Λ_{HeHe} cooling rate can be neglected.

Another important cooling mechanism is the excitation of low-lying states of C⁺, Si⁺, and Fe⁺ ions by electron impact. Once excited, these levels depopulate by downward radiative transitions, leading to an energy-loss rate Λ_{ei} . The presence of ions also gives rise to a heating, since the ions capture electrons, which are then ejected through photoionization by the galactic radiation field. This leads to an energy gain Γ_{ei} and an effective cooling rate $\Lambda_{ei} - \Gamma_{ei}$ due to the interaction of electrons with ions. The graph of $(\Lambda_{ei} - \Gamma_{ei})/n_{\rm H_2}$ as a function of temperature is shown in Figure 2. This curve is plotted from



FIG. 2.—Cooling rates as a function of temperature

the data given in Table 3 of TN. An element abundance ratio $n_{\rm H}: n_{\rm C}^+: n_{\rm Si}^+: n_{\rm Fe}^+ =$ 10^{6} :91:34:16 was assumed, along with a corresponding electron density $n_{e} = 2 \times 10^{-4}n_{\rm H}$. Also plotted in Figure 2 is the quantity $\Lambda_{\rm HH_2}/n_{\rm H}n_{\rm H_2}$ calculated from equation (25). It is seen that, for $n_{\rm H} = n_{\rm H_2}$ and the electron and ion abundances assumed, cooling by hydrogen molecules dominates above about 50° K. Below 50° K electron-ion excitations produce most of the cooling; this is due essentially to the low ($\Delta E/k = 92^{\circ}$ K) excitation energy of the level in C^+ . It might be remarked here that if the cosmic-ray ionization rate constant was very large, the cooling rate $\Lambda_{ei} - \Gamma_{ei}$ would be increased because of the resulting higher electron density. We shall return to the question of the cooling of H I clouds by hydrogen molecules in Paper II.

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