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QUANTUM THEORY OF HYDROGEN RECOMBINATION

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Abstract

A fully quantum mechanical treatment is presented of the three-body recombination process $H + H + {}^4\text{He} \rightarrow H_2 + {}^4\text{He}$ for $T = 1^\circ\text{K}$ where measurements have recently been performed. The calculation employs accurate interatomic potentials and thermal averaging. An impulse approximation is used to obtain the most important contributions to the rate constant. Off-shell effects are found to be important and are included in the final results which are in reasonable agreement with experiment. We find that the rate of formation of ortho- H_2 is substantially larger than that of para- H_2 . The magnetic field dependence of the recombination rate is also discussed.

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I. Introduction

Recent interest and experimental progress in the study of atomic hydrogen gas at temperatures below 1°K (1-3) has focused attention on the elementary chemical reaction $H + H + X \rightarrow H_2 + X$ where $X = \text{He}$, H or the wall of the container. The distinctive feature of this reaction at low temperatures is that the kinetic energy of the particles in the initial state is essentially zero compared to the binding energy of the final state. This fact severely limits the number of mechanisms by which the reaction can proceed. To see this, consider the problem of recombination at high temperatures, $T > 100^\circ\text{K}$. Experimental results for various buffer gases and references to the theoretical literature are given by Trainor *et al.* (4).

Two kinds of mechanisms are important at high temperature. We write these as

Process [1] is an exchange reaction. The assumption here is that there is an equilibrium number of HX molecules in the gas and that the rate limiting step is the exchange of an H -atom to form H_2 . The second process involves a similar line of reasoning. $(H_2)^*$ is a metastable "orbiting resonance" of the H_2 system. Such resonances can be formed in two-body collisions, and certain of these resonances have lifetimes which allow them to be in thermal equilibrium and to contribute significantly to recombination. This rather delicate point is discussed in more detail by Roberts, Bernstein and Curtiss (5).

Neither of processes [1] or [2] are possible at $T \leq 1.2^\circ\text{K}$ where

experiments have recently been performed (2). At 1°K any buffer gas or impurity has long since frozen out on the walls of the container except for H and He. Since H cannot bind to He, process [1] is excluded.

Resonant states (H_2)^{*} are also impossible at 1°K because their thermal probability is essentially zero. The lowest lying orbiting resonance, the $v = 14$, $L = 4$ state, is thought to be bound by $1.1 \pm 0.7^\circ K$ (6) and hence cannot contribute to process [2]. This leaves only the direct, three-body process by which recombination can occur.

Hardy *et al.* (2) report measurements of the recombination rate of hydrogen atoms in a closed glass tube of which the interior walls were coated with a thin film of superfluid 4He . The density n_{He} of the 4He atoms in the vapour above the film could be varied from $1 \times 10^{18} \text{ cm}^{-3}$ to $6 \times 10^{18} \text{ cm}^{-3}$ by varying the temperature from 0.98 to 1.24°K. The density of H-atoms was always in the range $3 \times 10^{10} < n_H < 2 \times 10^{12} \text{ cm}^{-3}$. Thus it is clear that, in any three-body collision involving two H-atoms, the third body was almost certain to be a 4He atom. It was also demonstrated that the binding of H-atoms to the surface of the liquid 4He film was unimportant for $0.98 < T < 1.24^\circ K$. Both the recombination rate and the hyperfine frequency shift extrapolated linearly to zero with the 4He vapor density n_{He} . These results suggest a binding energy of less than 1°K for H on liquid 4He as had been suggested by theoretical calculations (7). Quite recently Morrow *et al.* (8) have shown that this binding energy is $0.93 \pm 0.02^\circ K$.

The rate constant k obtained by Hardy *et al.* (2) is defined by

$$[3] \quad \frac{dn_H}{dt} = -k n_H^2 n_{He}$$

The experimental result was $k = (0.28 \pm 0.03) \times 10^{-32} \text{ cm}^6/\text{sec}$.

From quantum statistical mechanics we can write the rate constant as (9)

$$[4] \quad k = (2\pi)^7 \sum_{i,f} P_i |T_{i,f}|^2 \delta(\vec{p}_i - \vec{p}_f) \delta(E_i - E_f)$$

where P_i is the probability of the initial state and $T_{i,f}$ is the amplitude for scattering from an initial three-body state i into a final state f in which the two H-atoms are bound. In writing Eq. [4] in this form, we have made the assumption that the probability of the inverse process

is negligibly small because the probability of a He atom striking an H_2 molecule with enough energy to dissociate it is negligible. (We shall see that typical binding energies in the final state f are on the order of $10^2^\circ K$.)

The scattering amplitude $T_{i,f}$ has the form

$$[6] \quad T_{i,f}(\vec{k}_1, \vec{k}_2, \vec{k}_3; \vec{q}_3') = \langle \phi_f(1,2), \vec{q}_3' | U_{03} | \vec{k}_1, \vec{k}_2, \vec{k}_3 \rangle$$

where $\phi_f(1,2)$ is a bound state of H_2 , $\vec{q}_3'$ is the $H_2 - ^4He$ relative momentum (particle 3 is the 4He atom) and U_{03} is the $3 \rightarrow 2$ AGS amplitude (10,11). The aim of the present work is to calculate U_{03} , and hence the rate factor k .

In Sect. II we discuss the various atomic and molecular states which enter the calculation. The magnetic field dependence of the atomic H hyperfine states is given and coefficients are defined to describe the field dependence of the recombination rate.

In Sect. III we briefly review the appropriate three-body theory,

and derive the impulse approximation. In order to carry out the appropriate thermal average, it is necessary to make an analytic approximation to the half off-shell H-He t-matrix. This is discussed in Sect. IV. Section V contains the numerical results, and in the final section we review the situation vis-à-vis experiment. Several further experimental tests are proposed. In addition, there is considerable scope for theoretical development.

II. Atomic and molecular states and interatomic potentials

The atomic ground state of a hydrogen atom has zero orbital angular momentum, and hence the magnetic energy levels of the ground state atom depend only on the electron spin $\vec{s}$ and proton spin $\vec{I}$. The spin Hamiltonian is

$$[7] \quad H = H_0(\vec{f}_e \cdot \vec{s} + \vec{f}_p \cdot \vec{I}) + a \vec{I} \cdot \vec{s},$$

where $\vec{f}_e$ and $\vec{f}_p$ are the absolute values of the electron and proton gyromagnetic ratios, H_0 is the applied magnetic field which we take in the z-direction and a is the hyperfine constant of the H-atom, $a/h = 1420$ MHz ($a/k_B \approx 68$ mK). The hyperfine states $|n\rangle$, $n=1, \dots, 4$, of this Hamiltonian are, in order of increasing energy,

$$[8a] \quad |1\rangle = \cos \theta |+\uparrow\rangle - \sin \theta |+\downarrow\rangle$$

$$[8b] \quad |2\rangle = |+\uparrow\rangle$$

$$[8c] \quad |3\rangle = \sin \theta |+\uparrow\rangle + \cos \theta |+\downarrow\rangle$$

$$[8d] \quad |4\rangle = |+\downarrow\rangle$$

where $\tan 2\theta = a/[\hbar(\gamma_e + \gamma_p)H_0]$ and $\uparrow(\downarrow)$ refers to an electron (proton) spin. For $H_0 = 0$, states $|2\rangle$, $|3\rangle$ and $|4\rangle$ are degenerate and are separated from $|1\rangle$ by the energy a .

The H-H interatomic potential depends strongly on the total spin of the electrons, $\vec{S} = \vec{s}_1 + \vec{s}_2$, and is essentially independent of the total nuclear spin $\vec{I} = \vec{I}_1 + \vec{I}_2$. However the two-atom wave function must be separately antisymmetric in the electron and proton coordinates, and hence it is most convenient to work in a representation in which both $\vec{I}$ and $\vec{S}$ are specified. Thus we shall require coefficients of the type

$$[9] \quad A(h_1, h_2; I, M, S, N) = \langle h_1, h_2 | I, M, S, N \rangle$$

These coefficients are easily calculated in terms of Clebsch-Gordon coefficients and $\cos \theta$ and $\sin \theta$. We note that the hyperfine states $|h\rangle$ are eigenstates of $\vec{f}_z = \vec{I}_z + \vec{S}_z$ and that, although the magnitude of $\vec{f} = \vec{I} + \vec{S}$ is not a good quantum number, we can nevertheless label each state by f and f_z where f is total spin of the state for $H_0 = 0$. Then $|1\rangle = |0, 0\rangle$, $|2\rangle = |1, -1\rangle$, $|3\rangle = |1, 0\rangle$ and $|4\rangle = |1, 1\rangle$ and

$$[10] \quad \begin{aligned} & A(h_1, h_2; I, M, S, N) \\ &= A(f_1, m_1, f_2, m_2; I, M, S, N) \\ &= \delta_{m_1+m_2, M} + N A(f_1, m_1, f_2, m_2; I, M, S, N). \end{aligned}$$

Because the bound state of an H_2 molecule must have $S=N=0$ and because we will neglect the very small contributions to U_{03} which change I or S , we will only require the coefficients $|A(f_1, m_1, f_2, m_2; I, m_1+m_2, 0, 0)|^2$ which are listed in Table 1. These coefficients tell us which pairs of hyperfine states can decay into which final nuclear spin states and how the rate depends on field. The final molecular H_2 state is labelled by vibrational quantum number v , rotational quantum number L , and nuclear spin I . Because of the Pauli principle for protons, $L + I$ must be even. The allowed states are conventionally referred to as "ortho" ($I = 1$, L odd) and "para" ($I = 0$, L even) hydrogen.

In order to evaluate Eq. [4] for the rate constant k , it is necessary to specify the states i and f in complete detail. We write the initial state as

$$[11] \quad |i\rangle = P_S |\vec{k}_1, h_1, \vec{k}_2, h_2; \vec{k}_3\rangle$$

where $\vec{k}_1$ and $\vec{k}_2$ are the momenta of the two H-atoms, $\vec{h}_1$ and $\vec{h}_2$ are their hyperfine quantum numbers, and $\vec{k}_3$ is the momentum of the He atom, P_S is an operator which projects out a properly symmetrized, two H-atom state and will be defined in more detail below. We shall not symmetrize the wave function with respect to the electrons on the He-atom. Instead we shall treat the He atom as a single, distinguishable particle.

In terms of wave functions, the unsymmetrized two H-atom states may be written as

$$[12] \quad |\vec{k}_1, \vec{h}_1, \vec{k}_2, h_2\rangle = \chi_{h_1}(\vec{r}_1, \vec{s}_1) \chi_{h_2}(\vec{r}_2, \vec{s}_2) \phi(\vec{r}_1 - \vec{R}_1) \times \\ \times \phi(\vec{r}_2 - \vec{R}_2) e^{i\vec{k}_1 \cdot \vec{R}_1} e^{i\vec{k}_2 \cdot \vec{R}_2}$$

where $\vec{r}_1$ and $\vec{r}_2$ are electron spatial coordinates and $\vec{R}_1$ and $\vec{R}_2$ are proton spatial coordinates, χ_h is a hyperfine state of the type defined in Eq. [8], and ϕ is a hydrogen 1s wave function. A fully symmetrized two H-atom function is of the form

$$\begin{aligned} & \langle \vec{r}_1, \vec{r}_2, \vec{R}_1, \vec{R}_2 | \vec{Q}, \vec{q}; I, M, S, N \rangle = e^{i\vec{Q} \cdot (\vec{R}_1 + \vec{R}_2)} / 2 \phi_I^M \phi_S^N \times \\ & \times \frac{1}{\sqrt{2}} [\phi(\vec{r}_1 - \vec{R}_1) \phi(\vec{r}_2 - \vec{R}_2) + (-1)^S \phi(\vec{r}_1 - \vec{R}_2) \phi(\vec{r}_2 - \vec{R}_1)] \times \\ [13] \quad & \times \frac{1}{\sqrt{2}} [e^{i\vec{q} \cdot (\vec{R}_1 - \vec{R}_2)} + (-1)^{I+S} e^{i\vec{q} \cdot (\vec{R}_1 - \vec{R}_2)}] \end{aligned}$$

where $\vec{Q} = \vec{k}_1 + \vec{k}_2$, $\vec{q} = (\vec{k}_1 - \vec{k}_2)/2$ and ϕ_I^M and ϕ_S^N are respectively states of total proton and electron spin. Then the projection operator P_S may be written as

$$[14] \quad P_S = \frac{1}{2} \sum_{\vec{Q}, \vec{q}} \sum_{I, M, S, N} |\vec{Q}, \vec{q}; I, M, S, N\rangle \langle \vec{Q}, \vec{q}; I, M, S, N|.$$

The $\frac{1}{2}$ arises because terms in $\vec{q}$ and $-\vec{q}$ define identical states.

Using Eq. [14] in Eq. [11] for the initial state we find that

$$[15] \quad |i\rangle = \frac{1}{2} \sum_I A(f_1, m_1, f_2, m_2; I, m_1 + m_2, 0, 0) |\vec{Q}, \vec{q}; I, m_1 + m_2, 0, 0; \vec{k}_3\rangle$$

since we need only consider states with $S=N=0$. We must note here that the states of Eq. [12] correspond to only one half of the classically distinguishable states. If we represent the number of possible values of $(\vec{k}_1, \vec{k}_2)$ by N^2 , then there are $8N^2$ fully symmetrized pair states of the type defined in Eq. [13]. There are $16N^2$ states of the type defined in Eq. [12] and an equal number can be generated by interchanging electron space and spin coordinates in Eq. [12]. These $32N^2$ states can be decomposed into states which are fully symmetric, antisymmetric only in electron or proton coordinates, or fully antisymmetric in both electron and proton coordinates. Such considerations lead to an extra factor of 2 in the reaction rate as compared to what would be obtained if only the initial states specified by Eqs. [12] and [15] were used.

The final states are given by

$$[16] \quad |f\rangle = |\vec{p}_{12}, v, L, M_L, I, M_I; p_3\rangle$$

and are properly symmetrized if $L + I$ is required to be even. Combining Eqs. [4], [6], [15], and [16], we obtain an explicit expression for the total rate constant,

$$\begin{aligned}
& k = \frac{1}{2} (2\pi)^7 \sum_{\vec{k}_1, \vec{k}_2, \vec{k}_3} \sum_{h_1 h_2} P_H(\vec{k}_1) P_{He}(\vec{k}_2) P_{He}(\vec{k}_3) n_{h_1} n_{h_2} \times \\
& \times \sum_I |A(h_1, h_2; I, m_1 m_2, 0, 0)|^2 \sum_{\substack{\vec{p}_{12}, \vec{q}_3 \\ \vec{p}_{12}, \vec{q}_3}} \delta(\vec{k}_1 + \vec{k}_2 + \vec{k}_3 - \vec{p}_{12} - \vec{q}_3) \times \\
& \times \sum_{v, I, L, M_L} |\langle \vec{p}_{12}, v, L, M_L, I, m_1 m_2; q_3 | \times \\
& \times U_{03} | \vec{k}_1 + \vec{k}_2, \frac{1}{2}(\vec{k}_1 - \vec{k}_2), I, m_1 m_2, 0, 0; \vec{k}_3 \rangle | \delta(E_i - E_f),
\end{aligned}
\quad [17]$$

where P_H and P_{He} are the momentum distribution functions for H and He atoms and η_h is the fraction of H-atoms in hyperfine state h .

Equation [17] can be simplified considerably by factoring out all of the spin dependence and integrating out the centre-of-mass momentum, $\vec{p}_{12}$. It is useful to define the magnetic field dependent statistical factors

$$f_I = \sum_{h_1 h_2} \eta_{h_1} \eta_{h_2} |A(h_1, h_2; I, m_1 m_2, 0, 0)|^2 \quad [18]$$

using the values of the $|A|^2$ coefficients from Table 1, the f_I can be written as

$$f_0 = [(n_1^2 + n_3^2) \sin^2 2\theta + 2n_1 n_3 \cos^2 2\theta + 2n_2 n_4] / 4 \quad [19a]$$

$$f_1 = [1 - n_1^2 - n_2^2 - n_3^2 - n_4^2 - 2 \cos 2\theta (n_1 - n_3)(n_2 - n_4)] / 4 \quad [19b]$$

In the simplest case, in which all levels are equally populated, Eqs.

[19] give $f_0 = 1/16$ and $f_1 = 3/16$ independent of θ .

The Boltzmann factors in Eq. [17] have the form

$$P_X(p) \equiv P(m_X, p) = (\hbar^2 / 2\pi m_X kT)^{3/2} e^{-\hbar^2 p^2 / 2m_X kT} \quad [20]$$

where $x = H$ or ${}^4\text{He}$. The product of Boltzmann factors in [17] will thus involve the exponential of

$$\frac{k_1^2}{2m_H} + \frac{k_2^2}{2m_H} + \frac{k_3^2}{2m_{He}} = \frac{p^2}{2M} + \frac{q_3^2}{2\mu_3} + \frac{p_3^2}{2\mu_{12}} \quad [21]$$

where

$$\vec{p} = \vec{k}_1 + \vec{k}_2 + \vec{k}_3, \quad [22a]$$

$$p_3 = (\vec{k}_1 - \vec{k}_2) / 2, \quad [22b]$$

$$q_3 = [m_{He}(\vec{k}_1 + \vec{k}_2) - 2m_H \vec{k}_3] / M, \quad [22c]$$

and

$$M = 2m_H + m_{He}, \quad [23a]$$

$$\mu_{12}^{-1} = m_H^{-1} + m_H^{-1}, \quad \mu_3^{-1} = m_{He}^{-1} + (m_H + m_{He})^{-1}. \quad [23b]$$

Using Eqs. [20] and [21] we can rewrite the Boltzmann factors in terms of the total and relative momenta. Finally, since the matrix element of U_{03} is independent of p , one can integrate over this variable—thereby removing $P(M, \vec{p})$. The final expression for the transition rate [17] which will be used in the next section is therefore:

$$\begin{aligned}
dR = & \frac{(2\pi)^7}{2} \int d\vec{q}_3 \int d\vec{p}_3 P(\mu_3, \vec{q}_3) P(\mu_{12}, \vec{p}_3) \times \\
& \times \sum_{v, I, L, M_L} f_I \int d\vec{q}_3^2 \delta(q_3^2 / 2\mu_3 + p_3^2 / 2\mu_{12} + \epsilon_{v, L} - q_3'^2 / 2\mu_3) \times \\
& \times |\langle \vec{p}_3, \vec{q}_3; I | U_{03} | v, L, M_L, I; \vec{q}_3' \rangle|^2.
\end{aligned} \quad [24]$$

Equation [24] involves an eight dimensional integral, which clearly will be very difficult to evaluate even if U_{03} is a simple function.

III. Three-body calculation

The essential process which we must calculate is the three-body

(H + H + He) to two-body (H_2 + He) scattering amplitude illustrated in Fig. 1. There the cross-hatched line represents the molecular H_2 wave function, and particle 3 is the He atom. The initial three-body state is defined by any of the three pairs of c.m. momenta $(\vec{p}_1, \vec{q}_1)$ —c.f. Eq. [22]—where $\vec{p}_1$ is the relative momentum of pair 1, and $\vec{q}_1$ is the relative momentum of pair 1 with respect to particle 1. As usual we label the two-body potentials and t-matrices by the spectator index—eg.

$V(12) \equiv V_3$ etc. The exact transition operator in Fig. 1 is an AGS operator (10,11), U_{03} , defined through the usual three-body scattering equations

$$[25] \quad U_{ji}(E) = \bar{\delta}_{ji}(E-H_0) + \sum_{\ell(\neq i)=1}^3 U_{j\ell}(E) G_0(E) t_{\ell}(E).$$

In [25], H_0 is the free Hamiltonian of the three-body system and $G_0(E)$ the corresponding free Green's function. The adjoint delta is defined as

$$[26] \quad \bar{\delta}_{ji} = 1 - \delta_{ji},$$

and t_{ℓ} is the two-body t -matrix defined by the Lippmann-Schwinger equation

$$[27] \quad t_{\ell} = v_{\ell} + v_{\ell} G_0 t_{\ell}.$$

While the summation in [25] runs only from 1 to 3, so that it is a set of coupled equations between quasi-two-body states (spectator and pair), we may formally obtain the 3+2 operator by setting $j=0$ in [25],

$$[28] \quad U_{03}(E) = (E-H_0) + \sum_{\ell \neq 3} U_{0\ell}(E) G_0(E) t_{\ell}(E).$$

Iteration of Eq. [28] leads to the multiple scattering expansion

$$[29] \quad U_{03} = (E-H_0) + t_1 + t_2 + t_3 G_0(t_1+t_2) + (t_1 G_0 t_2 + t_2 G_0 t_1) + \dots$$

Since the three-body state is an eigenstate of H_0 of eigenvalue E , the $(E-H_0)$ term does not contribute to the physical (on energy-shell) scattering amplitude. If we further neglect all rescattering processes, we obtain the so-called impulse approximation

$$[30] \quad U_{03}^{IA} = t_1 + t_2,$$

which is used here.

The only real test of the impulse approximation is to solve exactly the coupled, two-dimensional integral equations which follow from [28] after partial wave decomposition. Such a calculation is a major effort, and in view of our results (to be presented in Sect. V) is a worthwhile Ph.D. project. We have reason to believe that higher order re-scattering effects may be significant at the 20% level—based on an estimate of the on-shell double scattering term, as discussed in Sect. VI.

Nevertheless there are a number of interesting theoretical features associated with the impulse approximation (such as the off-shell behaviour of the H-He t -matrix), which need to be understood before a full calculation is started. Moreover, it seems quite significant that, as we shall see, the present approximation does agree with experimental observation at the twenty to thirty percent level.

Given the impulse approximation [30], it is straightforward to write the appropriate matrix element of U_{03} . Using the momenta of Fig. 2 (in the three-body c.m.) we find, for a specific vibrational state (ν, I, L) with (momentum space) wave function $\phi_{LM_L}^I$,

$$U_{03} = \phi_{LM_L}^I \left(\frac{\vec{q}_3 - \vec{q}_3'}{2} + \vec{p}_3 \right) \lesssim \frac{3}{5} \vec{q}_3 - \frac{4}{5} \vec{p}_3 |t| \vec{q}_3' - \frac{2}{5} \vec{q}_3 - \frac{4}{5} \vec{p}_3 \rangle + [31] \quad + (-)^{I+S} \phi_{LM_L}^I \left(\frac{\vec{q}_3 - \vec{q}_3'}{2} - \vec{p}_3 \right) \lesssim \frac{3}{5} \vec{q}_3 + \frac{4}{5} \vec{p}_3 |t| \vec{q}_3' - \frac{2}{5} \vec{q}_3 + \frac{4}{5} \vec{p}_3 \rangle,$$

where $\lesssim$ on $p|t|p'$ is the half off-shell H-He t -matrix, with the on-shell energy defined by p . (This will be discussed in detail in Sect. IV.) In fact, to calculate a rate to a particular state (ν, I, L) we should perform the incoherent sum over the magnetic quantum numbers M_I and M_L . The partial recombination rate is then

$$\begin{aligned}
dR(v, I, L) = & \frac{(2\pi)^7}{2} f_I \frac{(2L+1)}{4\pi} \int d\vec{p}_3 \int d\vec{q}_3 P(u_{12}, \vec{p}_3) P(u_3, \vec{q}_3) \times \\
& \times \int d\vec{q}_3' \left(\frac{p_3^2}{2u_{12}} + \frac{q_3^2}{2u_3} - \frac{q_3'^2}{2u_3} + \epsilon_{2H}^{IL} \right) \times \\
& \times \left\{ \left| \phi_L^I \left(\frac{\vec{q}_3 - \vec{q}_3'}{2} + \vec{p}_3 \right) \right|_{\text{on } \frac{3}{5} q_3 - \frac{4}{5} p_3}^2 \left| t | \vec{q}_3' - \frac{2}{5} \vec{q}_3 - \frac{4}{5} \vec{p}_3 \rangle \right|^2 + \right. \\
& + \left| \phi_L^I \left(\frac{\vec{q}_3 - \vec{q}_3'}{2} - \vec{p}_3 \right) \right|_{\text{on } \frac{3}{5} q_3 + \frac{4}{5} p_3}^2 \left| t | \vec{q}_3' - \frac{2}{5} \vec{q}_3 + \frac{4}{5} \vec{p}_3 \rangle \right|^2 + \\
& + 2P_L \left(\frac{\vec{q}_3 - \vec{q}_3'}{2} + \vec{p}_3 \cdot \vec{p}_3 \right) \left[\frac{\vec{q}_3 - \vec{q}_3'}{2} \right] \text{Re} \left[\phi_L^I \left(\frac{\vec{q}_3 - \vec{q}_3'}{2} + \vec{p}_3 \right) \right] \times \\
& \times \phi_L^{I*} \left(\frac{\vec{q}_3 - \vec{q}_3'}{2} - \vec{p}_3 \right) \Big|_{\text{on } \frac{3}{5} q_3 - \frac{4}{5} p_3} \left| t | \vec{q}_3' - \frac{2}{5} \vec{q}_3 - \frac{4}{5} \vec{p}_3 \rangle \right| \times \\
& \times \Big|_{\text{on } \frac{3}{5} q_3 + \frac{4}{5} p_3} \left| t | \vec{q}_3' - \frac{2}{5} \vec{q}_3 + \frac{4}{5} \vec{p}_3 \rangle \right| \Big\}^*,
\end{aligned}
\quad [32]$$

where we have used the result of Sect. II that $I + L + S$ should be even.

Since there is usually considerable energy release in the recombination process, q_3' will be considerably larger than (p_3, q_3) . Thus the P_L factor will be about +1 for L even, and -1 for L odd. Therefore, in the extreme low temperature, large binding energy limit, $|u_3|^2$ will be $4|t\phi|^2$ if L is even, and zero if L is odd. For finite temperature it is essential to carry out the thermal averaging implied by [32]. It is clear that the effect of such averaging will be to lower the transition rate to para- H_2 states from the limit quoted above, and more importantly to give a non-zero rate of ortho- H_2 formation. Indeed, as we shall see the calculations at 1°K indicate that the latter dominates.

IV. Evaluation of the off-shell H-He t-matrix

The two-body t-matrix is defined as the solution of the Lippmann-Schwinger equation

$$\begin{aligned}
\langle \vec{q} | t(E) | \vec{q}' \rangle = & \langle \vec{q} | V | \vec{q}' \rangle + \int d\vec{q}'' \langle \vec{q} | V | \vec{q}'' \rangle \times \\
& \times (E^+ - q''^2/2\mu)^{-1} \langle \vec{q}'' | t(E) | \vec{q}' \rangle,
\end{aligned}
\quad [33]$$

where $\langle \vec{q} | V | \vec{q}' \rangle$ ($= V(\vec{q} - \vec{q}')$) in the H-He case) is the Fourier transform of the potential. Equation [33] defines t for arbitrary q, q' and E .

In the case where $q = q' = (2\mu E)^{1/2} \equiv q_E$, that is *on-energy-shell*, the t-matrix in a given partial wave:

$$\langle \vec{q} | t(E) | \vec{q}' \rangle = (4\pi)^{-1} \sum_{\ell} (2\ell+1) t_{\ell}(q, q'; E) P_{\ell}(\hat{q} \cdot \hat{q}'), \quad [34]$$

is directly related to the phase shift

$$t_{\ell}(q_E, q_E; E) = - \frac{e^{i\delta_{\ell}} \sin \delta_{\ell}}{\pi \mu q_E}. \quad [35]$$

Using a partial wave expansion for $V(\vec{q} - \vec{q}')$ similar to that for t

in [34] that is

$$V_{\ell}(q, q') = 2\pi \int_{-1}^{+1} d(\cos \theta) P_{\ell}(\cos \theta) V(\vec{q} - \vec{q}'), \quad [36]$$

Eq. [33] can be reduced to a one dimensional integral equation

$$t_{\ell}(q, q'; E) = V_{\ell}(q, q') + \int_0^{\infty} dq'' q''^2 \frac{V_{\ell}(q, q'') t_{\ell}(q'', q'; E)}{E^+ - q''^2/2\mu} \quad [37]$$

With some algebra, one can use the structure of this equation to prove that the half off-shell (either q or q' equals q_E , but not both) t-matrix can always be written as (10, 12)

$$t_{\ell}(q_E, q; E) = f_{\ell}(E, q) t_{\ell}(q_E, q_E; E), \quad [38]$$

where $f_{\ell}(E, q)$ is the Kowalski-Moyes half shell function, which equals one when $q = q_E$, and is *real*. In fact, it is possible to obtain an equation directly for $f_{\ell}(E, q)$,

$$f_{\ell}(E, q) = \text{Re} \left\{ \frac{1}{t_{\ell}(E)} \right\} V_{\ell}(q, q_E) + \int dq'' q''^2 \frac{V_{\ell}(q, q'') f_{\ell}(E, q'')}{E - q''^2/2\mu}. \quad [39]$$

The P indicates a principal value integral, and therefore [39] is a purely real equation.

In the present work we solve Eq. [39] directly for $f_\ell(E, q)/\text{Re}\{1/t_\ell(q_E, q_E; E)\}$. We can also use the fact that $f_\ell(E, q_E) = 1$ to obtain $\text{Re}\{1/t_\ell(q_E, q_E; E)\}$, and through Eq. [35] the phase shift. The H-He potential is parametrized as:

$$\begin{aligned}
 V(r) &= Ae^{-\alpha r} - A_0 \quad r < \sigma \\
 &= \epsilon f[(\sigma/r)^{12} - (\sigma/r)^6] \quad \sigma < r < r_C \\
 &= -f[c_6/r^6 + c_8/r^8 + c_{10}/r^{10}] \quad r > r_C,
 \end{aligned}
 \quad [40]$$

where

$$\begin{aligned}
 A &= 70 \text{ eV}; \quad A_0 = Ae^{-\alpha\sigma}; \quad \alpha = 3.383 \text{ \AA}^{-1}; \quad \epsilon = 2.392 \times 10^{-3} \text{ eV}; \\
 f &= 1.06; \quad \sigma = 3.26 \text{ \AA}; \quad r_C = 4.071 \text{ \AA}; \quad c_6 = 1.691 \text{ eV-\AA}^6; \\
 c_8 &= 7.011 \text{ eV-\AA}^8; \quad c_{10} = 0.
 \end{aligned}
 \quad [41]$$

Since the hard core is by far the largest piece of this potential (99.5% of the volume integral), it must be Fourier transformed very carefully. Fortunately this can be done analytically—let us call the result $V^0(q)$:

$$\begin{aligned}
 V^0(q) &= \frac{A}{2\pi^2 q} \left[\frac{2q\alpha}{(q^2 + \alpha^2)^2} - \frac{e^{-\sigma\alpha}}{(q^2 + \alpha^2)^2} \right] 2q\alpha \cos(q\sigma) + \\
 &\quad + (\alpha^2 - q^2) \sin(q\sigma) \left\{ -\frac{\sigma\alpha e^{-\sigma\alpha}}{q^2 + \alpha^2} \frac{q}{\alpha} \cos(q\sigma) + \sin(q\sigma) \right\} + \\
 &\quad + e^{-\sigma\alpha} \left\{ \frac{\alpha}{q} \cos(q\sigma) - \frac{\sin(q\sigma)}{q^2} \right\}.
 \end{aligned}
 \quad [42]$$

The rest of $V(q)$ is obtained numerically, as is its partial wave expansion. The partial wave expansion of the first piece of $V^0(q)$ could be found analytically, which greatly enhanced the computational accuracy.

In Fig. 3 we present the results of our calculation of the half-shell function $f_0(E, q)$ at several energies. The p-wave half off-shell t-matrix $t_1(q_E, q; E)$ is shown in Fig. 4. In both cases the half-shell function behaves as a damped oscillator. (Note that the typical on-shell energy for the recombination process is $E = 0.09 \text{ meV}$, corresponding to an on-shell momentum of $0.19 \text{ \AA}^{-1}$.)

Although Fig. 3 may give the impression that t_0 depends strongly on energy, this is not the case. If we multiply by the on-shell t-matrix, all of the curves in Fig. 3 tend to coincide. Indeed we plotted f_0 rather than t_0 in order to make the curves more readily distinguishable. Even for $\ell = 1$, where there is a certain energy dependence, the shape is basically independent of energy. Consequently we have parametrized the t-matrices as follows. For $\ell = 0$ we take

$$t_0(q_E, q; E) \approx e^{i\delta_0(E)} |t_0(q_E, q_E; \bar{E})| f_0(\bar{E}, q),
 \quad [43]$$

and for $\ell = 1$ we use,

$$t_1(q_E, q; E) \approx -e^{i\delta_1(E)} |t_1(q_E, q_E; \bar{E})| f_1(\bar{E}, q) g(E),
 \quad [44]$$

where $\bar{E}$ is a fixed energy such that $q_E = 0.183 \text{ \AA}^{-1}$. In [44] $g(E)$ is a real function which renormalizes the on-shell t-matrix at $\bar{E}$ to that at E . The functions $f_\ell(\bar{E}, q)$ have been fitted to the numerical results of Figs. 3 and 4 with an accuracy better than one percent.

The s- and p-wave phase shifts are shown in Figs. 5 and 6. They can be parametrized as

$$\delta_0(E) = -18.0 \text{ } q_E^3 / (1 + 2.48(q_E - q_E) + 13.5(q_E - q_E)^2),
 \quad [45]$$

$$\delta_1(E) = 8.0 \text{ } q_E^3 / (1 + 4.94(q_E - q_E) + 22.8(q_E - q_E)^2).
 \quad [46]$$

We observe that it is a peculiarity of the H-He potential that $\delta_0(E)$

only has the usual linear dependence on q_E for an extremely small range of q_E near zero. This anomalous behaviour leads to a strong suppression of the s-wave contribution, and therefore to a strong increase in the relative importance of p-wave scattering.

V. Results

Once one has calculated the half off-shell H-He t-matrix as described in Sect. IV, and also solved the Schrödinger equation for the vibrational state wave functions, all that remains to be done to obtain a partial recombination rate is to evaluate the eight-dimensional integral in Eq. [32]! In fact, three angular integrations can be carried out trivially, but the remaining five-dimensional integral is very time consuming. In order that this calculation takes a reasonable amount of computer time—even for impulse approximation—it was necessary to make analytic approximations for the half off-shell t-matrices (Sect. IV), and also for the vibrational wave functions. A numerical accuracy of better than 1% was obtained using eight point Gaussian quadrature for the angular integrations, and 5 point Laguerre quadrature for the integral over the energy ($p_3^2/2\mu_{12} + q_3^2/2\mu_3$).

Of course, this problem is very much simplified in the low temperature, large binding energy limit. In fact, in that limit (see Sect. III) the matrix element of U_{03} vanishes for ortho- H_2 , and reduces to $\langle 2 \phi(q_3/2) | \hat{O} | t | q_3 \rangle$ for para- H_2 . Then, only trivial integrations remain to be done in order to obtain the recombination rate. Preliminary calculations using this approximation were presented at the Few Body Conference in Eugene (13). Unfortunately the *thermal averaging* is so important, that such a calculation is not quantitatively reliable—even for para- H_2 . For formation of ortho- H_2 it is quite wrong.

Table 2 shows the calculated recombination rates (in units of 10^{-34} cm⁶/sec) for the least bound states of the H_2 system. (The recombination rate for any more deeply bound vibrational state is negligible at these temperatures because of the enormous momentum mismatch.) At 1°K the experimental recombination rate is 28×10^{-34} cm⁶/sec, which should be compared with the sum of the theoretically calculated rates to all states—that is 18×10^{-34} cm⁶/sec. More than 80% of this recombination occurs via the $v = 14$, $L = 3$ ortho- H_2 state.

The calculation has also been carried out at 0.1°K and 0.01°K, and these results serve to emphasize the importance of thermal averaging for the ortho- H_2 rate. In fact that recombination rate drops an order of magnitude for each order of magnitude decrease in temperature—in contrast with the para- H_2 recombination rate, which is quite slowly decreasing. This behaviour can be understood very simply because the integral in Eq. [32] behaves like q_3^2 , which gives rise to a linear temperature dependence.

VI. Discussion

We have made detailed calculations of the rate of recombination of atomic hydrogen through the true three-body reaction

The calculated rate constant of $k_{th} = 18 \times 10^{-34}$ cm⁶/sec at 1°K is in remarkably good agreement with the experimental determination of $k = 28 \times 10^{-34}$ cm⁶/sec (2). Most of this recombination occurs through the formation of ortho- H_2 . As a consequence we predict a very strong temperature dependence for k .

The impulse approximation was used for reaction [47]. In practice, the overwhelming importance of thermal averaging suggests that it may

not be possible to improve the approximation for U_{03} , and still perform the calculation in a finite time. Nevertheless, one should still ask how good the impulse approximation is expected to be on theoretical grounds. One indication can be obtained by considering the on-shell piece of the double scattering term in [29]. It is quite easy to show that including the on-shell piece of the double scattering term leads to the replacement (schematically)

$$[48] \quad t_1 \rightarrow (1 + i e^{i\delta_3} \sin\delta_3 + i e^{i\delta_j} \sin\delta_j) t_1; \quad i \neq j = 1, 2.$$

(Here δ_3 is the H-H phase shift, and δ_j the H-He phase shift, at the appropriate on-shell energy.)

If we ignore thermal averaging this leads to less than a 1% decrease in the transition rate. However, since the main contribution comes from $v = 14$, $L = 3$, and relies heavily on a lack of cancellation between $\phi_{11}t_1$ and $\phi_{21}t_2$, this additional phase will increase the ortho-H₂ rate. In fact, we find that the $L = 3$ rate, through s-wave H-He scattering, is increased by about 3×10^{-34} cm⁶/sec. Thus the on-shell double scattering term already significantly bridges the gap between theory and experiment. Ultimately one would like to check this against a full solution of the exact, coupled, two-dimensional integral equations for U .

Experimental verification of the details of our theory awaits measurements of the temperature dependence of the recombination rate constant. This measurement is quite difficult to obtain for a container coated with liquid ⁴He because wall recombination becomes important below about 0.7°K. However for ³He-coated surfaces, the binding energy is much smaller and bulk recombination dominates down to about 0.3°K (14).

At low temperature and high magnetic field H , the hyperfine populations n_3 and n_4 can be made negligibly small. Then both f_0 and f_1 are proportional to H_0^{-2} because θ , defined below Eq. [8], is proportional to H_0^{-1} . Specifically for $n_3 = n_4 = 0$ and $\theta \ll 1$ we have

$$[49a] \quad f_0 \approx n_1^2 \theta^2$$

$$[49b] \quad f_1 \approx n_1 n_2 \theta^2$$

and

$$[50] \quad \theta \approx a/(2\hbar\gamma_e H_0).$$

We expect f_0 and f_1 to scale the para- and ortho-hydrogen formation rates for all processes which involve only two H-atoms. In particular they should scale the wall process which dominates the recombination rate for ⁴He-coated walls below 0.7°K. This expectation has recently received strong experimental support from measurements by Matthey *et al.* (15) who confirm the H_0^{-2} dependence of the recombination rate. A quantitative comparison of their results to the $H_0 = 0$ results of ref. (8) is also quite consistent with the predictions of Eqs. [49] and [50].

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Table 1. The coefficients $|A(F_1, M_1, F_2, M_2; I, M_1 + M_2, 0, 0)|^2$

	(a) $I=0$			
	(0,0) ^a	(1,-1)	(1,0)	(1,1)
(0,0) ^a	$\sin^2\theta \cos^2\theta$	0	$\frac{1}{4}(\cos^2\theta - \sin^2\theta)^2$	0
(1,-1)	0	0	0	$\frac{1}{4}$
(1,0)	$\frac{1}{4}(\cos^2\theta - \sin^2\theta)^2$	0	$\sin^2\theta \cos^2\theta$	0
(1,1)	0	$\frac{1}{4}$	0	0

(b) $I=1$

	(0,0) ^a	(1,-1)	(1,0)	(1,1)
(0,0) ^a	0	$\frac{1}{2} \sin^2\theta$	$\frac{1}{4}$	$\frac{1}{2} \cos^2\theta$
(1,-1)	$\frac{1}{2} \sin^2\theta$	0	$\frac{1}{2} \cos^2\theta$	$\frac{1}{4}$
(1,0)	$\frac{1}{4}$	$\frac{1}{2} \cos^2\theta$	0	$\frac{1}{2} \sin^2\theta$
(1,1)	$\frac{1}{2} \cos^2\theta$	$\frac{1}{4}$	$\frac{1}{2} \sin^2\theta$	0

^aRows and columns are labelled by (F_1, M_1) and (F_2, M_2) .

Table 2. Listed are the contributions of different states (characterized by angular momentum and energy) to the recombination rate. The results are given in units of 10^{-34} cm⁶/sec. The experimental value in these units is 28. Both results using the s-wave H-He t-matrix, and the s- and p-wave H-He t-matrix are given. For 0.1°K and 0.01°K we only show the states which are expected to contribute most.

L	$\epsilon(\text{cm}^{-1})$	1°K s	s + p	0.1°K s + p	0.01°K s + p
0	146.2	0.059	0.095	0.056	0.049
1	128.7	0.065	0.183	0.016	
2	96.3	0.904	1.747	1.32	1.29
3	51.1	10.37	14.63	1.62	0.147
4	1.0	0.943	1.107	0.0015	
7	52.97	0.014	0.025		
Total		12.36	17.79	3.01	1.49
Experimental		28 ± 3	28 ± 3		

Figure Captions

Fig. 1. The three-body recombination mechanism calculated here.

Fig. 2. The two contributions to the three-body recombination process in impulse approximation.

Fig. 3. Half off-shell function for s-wave H-He scattering at three energies.

Fig. 4. Half off-shell t-matrix, $t_1(k, k; E)$, for p-wave H-He scattering at three energies.

Fig. 5. The s-wave H-He phase shift as a function of energy.

Fig. 6. The p-wave H-He phase shift as a function of energy.

Fig. 1

Fig. 2

Fig. 3

Fig. 4