MOLECULAR HYDROGEN FORMATION BY EXCITED ATOM RADIATIVE ASSOCIATION

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ABSTRACT

The results from a semiclassical calculation of the thermal rate coefficient for the radiative association process $H(n = 2) + H(n = 1) \rightarrow H_2 + h\nu$ are presented (n is the principal quantum number of the separated hydrogen atoms). The relative importance of this reaction in various environments is briefly discussed. Models of the early universe around the epoch of recombination and protostellar winds have been calculated which include the excited atom process. Not surprisingly, it is shown that the excited atom process will not be important in the general interstellar medium, except possibly in environments where the amount of Lyα photon trapping is large. Examples may be the material surrounding quasars, active galactic nuclei, and bright H II regions. The most likely application of this process might be within rapidly evolving systems where a large transient $n = 2$ population of neutral hydrogen could result in a burst of molecular hydrogen formation.

Subject headings: interstellar: molecules — molecular processes

1. INTRODUCTION

At densities typical of the general interstellar medium, molecule formation by radiative association,

$$A + B \rightleftarrows AB^* \rightarrow AB + h\nu , \qquad (1)$$

might compete with other processes in the gas phase. As a result, the determination of rate coefficients for radiative association is important to the accurate analysis of molecule formation and destruction processes in astrophysics. In conventional usage, the rate of a reaction per unit volume per unit time is given by $kn(A)n(B)$ cm^{-3} s^{-1}, where k is the rate coefficient in cm^3 s^{-1} and $n(A)$ and $n(B)$ are number densities of species A and B in cm^{-3}.

In a classical treatment of radiative association, the colliding particles, which can be atoms, molecules, or ions, approach along a potential energy curve of the resultant molecule. This curve can be a repulsive (unbound) molecular state or, as is required for rapid low-temperature association, that of a bound state. Stabilization of the separated pair into a bound molecule will occur if the system can radiate a photon of energy $h\nu \geq E_{coll}$ (E_{coll} = total center of mass energy of the colliding pair) during the interaction, such that energy and angular momentum of the system are conserved without a third body. This process is, in general, inefficient, since the collision time (on the order of a molecular vibrational period, 10^{-13} s) must be weighted against the inverse of the radiative lifetime (the transition probability) of the stabilizing transition. The radiative lifetime can range from ≈ 1 ns for allowed electronic transitions in the ultraviolet to 10^{-3} to 10^{-2} s for intrinsically weak vibrational transitions (van Dishoeck 1989). Thus, the rate of radiative association will be enhanced if the emission of a stabilizing photon is due to a strong electronic transition.

The usual selection rules for a transition resulting in radiative association must be followed. For homonuclear molecules it is required that even states combine only with odd:

$$g \leftrightarrow u , \quad g \not\leftrightarrow g , \quad u \not\leftrightarrow u . \qquad (2)$$
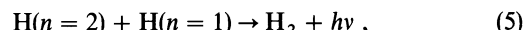
In addition,

$$\Delta S = 0 , \quad \Delta\Lambda = 0, \pm 1 , \qquad (3)$$
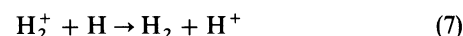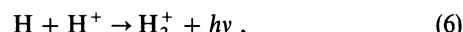
and

$$\Sigma^+ \leftrightarrow \Sigma^+ , \quad \Sigma^- \leftrightarrow \Sigma^- , \qquad (4)$$

but Σ^+ states *cannot* combine with Σ^- states. Additional selection rules for more general transitions may be found in Herzberg (1950).
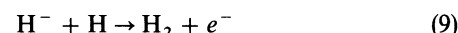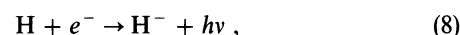
In this paper we discuss the semiclassical determination of a radiative rate coefficient for the excited atom process

$$H(n = 2) + H(n = 1) \rightarrow H_2 + h\nu , \qquad (5)$$

where n is the principal quantum number of the separated hydrogen atoms. Association of ground-state atoms is negligible because there are no allowed stabilizing transitions. In most interstellar environments, association catalyzed on grain surfaces is thought to dominate the formation of H_2; however, in regions where surface reactions are not important, the "standard" gas-phase processes

$$H + H^+ \rightarrow H_2^+ + h\nu , \qquad (6)$$

$$H_2^+ + H \rightarrow H_2 + H^+ \qquad (7)$$

(the H_2^+ process) and

$$H + e^- \rightarrow H^- + h\nu , \qquad (8)$$

$$H^- + H \rightarrow H_2 + e^- \qquad (9)$$

(the H^- process) will be the dominant routes to the formation of H_2. However, conditions may arise such that the population of hydrogen in the $n = 2$ state is large enough for reaction (5) to be a significant source of molecular hydrogen. In the final section we consider possible applications of reaction (5), and assess the overall contribution of the excited atom process in some specific cases. First, we describe the method of calculation and present the results.

2. METHOD OF CALCULATION

We use the semiclassical method of Bates (1951). Such an approach is valid in the case of massive reactants or strong stabilizing transitions. It ignores the possible low-temperature

effects of tunneling and shape resonances. In this approx-imation, the radiative rate coefficient for a Maxwellian dis-tribution of particle velocities is given by

$$k = 8\sqrt{\pi}\, g \iint A(r) r^2 e^{-\epsilon} \left[\xi^{1/2} - \left(\xi - \epsilon\, \frac{b_m^2}{r^2} \right)^{1/2} \right] d\epsilon\, dr\, , \quad (10)$$

where

$$\epsilon = \frac{\mu v^2}{2kT}\, , \quad \xi = \epsilon - \frac{U'(r)}{kT}\, , \quad (11)$$

$U'(r)$ is the initial, or upper-state, potential curve, and μ is the reduced mass of the reactants ($\mu = m_1^{-1} + m_2^{-1}$). The greatest value of the impact parameter for a specific internuclear separation r and relative velocity v at which association may occur is b_m. The factor g is the ratio of the statistical weight for the initial molecular state to the sum of statistical weights for all possible molecular states that dissociate to the same separated atom states:

$$g = g'(\Lambda', S') / \textstyle\sum_{\text{states}} g_i(\Lambda_i, S_i)\, ,$$
$$g_i(\Lambda_i, S_i) = (2S_i + 1)(2 - \delta_{0,\Lambda_i})\, . \quad (12)$$

The transition probability is given by its usual form (see Larsson 1983):

$$A(r) = \frac{64\pi^4 \Theta}{3h^4 c^3} |R(r)|^2 [U'(r) - U''(r)]^3 \text{ s}^{-1}\, . \quad (13)$$

Here $R(r) = \langle \psi'_e | M_e(r) | \psi''_e \rangle$ is the electronic transition moment, $M_e(r)$ is the dipole transition moment function, $U''(r)$ is the ground-, or lower, state potential curve, and Θ is given by

$$\Theta = \frac{2 - \delta_{0,\Lambda' + \Lambda''}}{2 - \delta_{0,\Lambda'}}\, . \quad (14)$$

It is important to note that if $U'(r)$ is positive everywhere, or falls off as, or more slowly than, r^{-2}, then the second term inside the brackets in equation (10) is identically zero by the laws of motion. However, in the most general case, $U'(r)$ falls off faster than r^{-2}. Indeed, for most bound molecular poten-tials this will be true. As a result, an explicit value of b_m must be found in the domain of r and ϵ where this term is nonzero (see Bates 1951 for a detailed discussion). Generally, the integra-tions in equation (10) are performed numerically with limits on r from the classical turning point r' to ∞ (see below, however). The lower bound on ϵ is zero where $U'(r)$ is negative and $U'(r)/kT$ where $U'(r)$ is positive. The upper bound on ϵ is $[U'(r) - U''(r)]/kT$.

3. RESULTS

As an illustration, we will first make an order-of-magnitude estimate for the rate of reaction (5). The radiative rate coeffi-cient can be expressed as the collision rate (σv cm^3 s^{-1}) weighted by the probability that a stabilizing transition can occur during the encounter. That probability is $P = A_{ul}\delta t$, where $\delta t = d/v$ is the collision time and d is the distance over which an interaction can take place (≈ 1 Å). Taking the tem-perature to be ≈ 500 K, we find $P \approx 3.3 \times 10^{-5}$ ($A_{ul} \approx 10^9$ s^{-1}) and a collision rate of $\approx 4.0 \times 10^{-10}$ cm^3 s^{-1}. Thus, the radiative rate coefficient should be of the order $k \sim 10^{-14}$ cm^3 s^{-1}. The relatively large value for this rate coefficient is due to the strength of the stabilizing transition. In general, however,

the $n = 2$ population will be low, and this process will be inef-fective.

There are three potential curves with allowed transitions to the X $^1\Sigma_g^+$ ground state of H_2 which correlate with atomic hydrogen in $n = 2$ and $n = 1$. The potential curves of the B $^1\Sigma_u^+$ and C $^1\Pi_u$ states correlate with $H(2p)$ and $H(1s)$. The potential curve of the B' $^1\Sigma_u^+$ state correlates with $H(2s)$ and $H(1s)$ (Fig. 1). The potentials used are taken from Stephens & Dalgarno (1972, 1974), Kołos (1975, 1976), Kołos & Wolnie-wicz (1975), Kołos & Rychlewski (1976), Kołos, Szalewicz & Monkhorst (1986), and Kwok, Dalgarno, & Posen (1985). The transition moments are from Ford et al. (1975), Dressler & Wolniewicz (1985), and Kwok et al. (1985). The statistical weight factors are $g = 1/24$ for B $^1\Sigma_u^+ \to X$ $^1\Sigma_g^+$, $g = 2/24$ for C $^1\Pi_u \to X$ $^1\Sigma_g^+$, $g = 1/8$ for B' $^1\Sigma_u^+ \to X$ $^1\Sigma_g^+$, and $\Theta = 1$ (cf. Sharp 1971).

Since the transition probabilities for the B $^1\Sigma_u^+ \to X$ $^1\Sigma_g^+$ and C $^1\Pi_u \to X$ $^1\Sigma_g^+$ transitions do not tend to zero as r goes to infinity, but go to the separated atom values for the Lyα tran-sition, a maximum internuclear separation for which associ-ation is probable must be determined. A maximum value of r beyond which association will not occur can be found in terms of a probability in the following way. We must first note that the highest bound vibration-rotation level in the ground elec-tronic state of H_2 is $v = 14$, $J = 4$. If tunneling is ignored (implicit in the Bates method), the maximum value of r is just the classical turning point of the $v = 14$, $J = 0$ level in the X $^1\Sigma_g^+$ ground state of H_2, namely, 6.140 bohr. The corre-sponding distance for $J = 4$ is 9.058 bohr. That is, if a photon is emitted while r is greater than the classical turning point of the highest bound level, the transition is not stabilizing and no molecule will be formed.

Classically, the rotation of the resultant molecule will depend on the impact parameter of the collision. If the impact parameter is zero, then $J = 0$. If the impact parameter is large, then J will tend to 4. The internuclear separation of the clas-sical turning point for $v = 14$ increases approximately linearly with J (or impact parameter). If a transition to the molecular ground electronic state occurs at an internuclear separation $r \leq 6.140$ bohr, then the probability that a bound state will
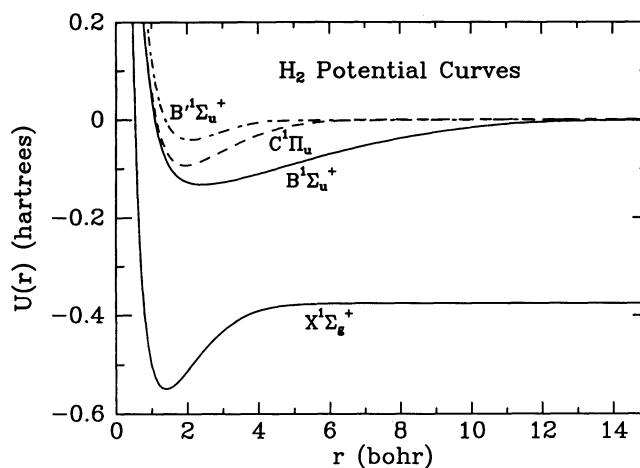

FIG. 1.—Molecular hydrogen potential energy curves which identify the primary routes for the excited atom radiative association process to form molecular hydrogen (reaction [5]). The B' $^1\Sigma_u^+$ state correlates with $H(2s)$ and $H(1s)$ at large internuclear separations. The potential curves of the B $^1\Sigma_u^+$ and C $^1\Pi_u$ states correlate with $H(2p)$ and $H(1s)$.

TABLE 1

RADIATIVE ASSOCIATION

$H(n = 2) + H(n = 1) \rightarrow H_2 + h\nu$

TEMPERATURE (K)	RATE COEFFICIENT ($\times 10^{-14}$ cm³ s⁻¹)	
	k_{2s}	k_{2p}
50	2.7	0.93
100	2.2	1.2
500	1.4	2.7
1000	1.2	3.4
2500	1.2	4.1
5000	1.1	4.3
10000	1.1	4.2
30000	1.0	3.6

result is unity. Conversely, for $r > 9.058$ bohr, all transitions will lead to an unbound molecular state. As r decreases toward 6.140 bohr, the range in impact parameter over which a transition is stabilizing increases. This means that the probability of a bound state forming increases from zero for transitions which occur beyond $r = 9.058$ bohr, to unity for transitions which occur within $r = 6.140$ bohr. Therefore, a linear probability function for association over the range $6.014 < r \le 9.058$ bohr should provide an adequate representation. The integration over r is carried out to an upper bound of $r_m = 9.058$ bohr. A probability function which decreases from unity to zero over the range $6.140 < r \le 9.058$ bohr has been applied, thereby limiting the range of internuclear separation over which a stabilizing transition can take place.

Our results for transitions from each of the three upper states are listed in Table 1 and displayed graphically in Figure 2. The rate coefficients are presented as $k_{2p} = k(B\ {}^1\Sigma_u^+) + k(C\ {}^1\Pi_u)$ and $k_{2s} = k(B\ {}^1\Sigma_u^+)$. For statistical populations in the atomic hydrogen 2s and 2p states, the total rate coefficient is $k_{H*} = (3k_{2p} + k_{2s})/4$. The excited atom formation rate is then $R(H*) = k_{H*} n(H_{n=2}) n(H_{1s})$ cm⁻³ s⁻¹.
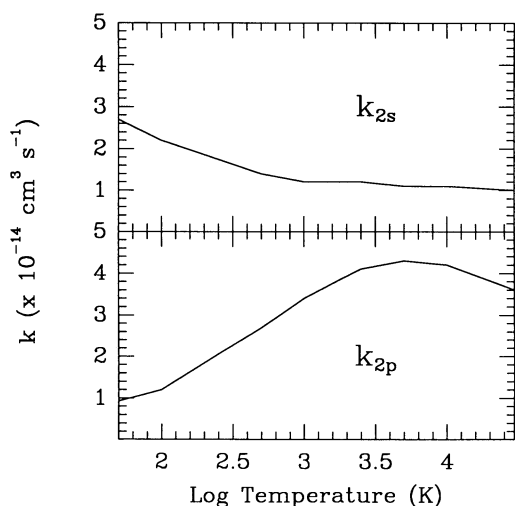

FIG. 2.—Graphical representation of the calculated rate coefficients for reaction (5), which are also listed in Table 1. The rate coefficient k_{2s} is for radiative association through the molecular potential which correlates to the atomic levels 2s and 1s ($B'\ {}^1\Sigma_u^+$), and k_{2p} is the rate coefficient for radiative association through the molecular potentials which correlate to the atomic levels 2p and 1s ($B\ {}^1\Sigma_u^+$ and $C\ {}^1\Pi_u$).

4. DISCUSSION

In what follows, we will examine the relative importance of reaction (5) compared with other gas-phase processes which form H_2 in a number of typical environments. Since reaction (5) requires the presence of a significant atomic hydrogen $n = 2$ population, it clearly will not be important throughout most of the general interstellar medium.

In local thermodynamic equilibriun (LTE), a system is defined by one unique temperature. In addition, the ionization fraction and level populations are determined by the Saha and Boltzmann equations, respectively. Of course, it is not in general necessary to consider individual processes in LTE. Nonetheless, it may be instructive to know what reactions are dominant under various conditions. For a gas in LTE, which consists only of hydrogen, it is straightforward to show that the rate of H_2 formation by reaction (5) [$R(H*)$ cm⁻³ s⁻¹] compared with the associative detachment process [reaction (9); $R(H^-)$ cm⁻³ s⁻¹] is

$$n_{H^0}^{1/2} Q^{-3/2}(H) \frac{R(H*)}{R(H^-)} = \begin{cases} 1.4 \times 10^1 , & T = 4000\ \text{K} , \\ 1.9 \times 10^2 , & T = 5000\ \text{K} , \\ 6.2 \times 10^3 , & T = 7500\ \text{K} , \\ 3.8 \times 10^4 , & T = 10,000\ \text{K} . \end{cases} \quad (15)$$

$Q(H)$ is the atomic hydrogen partition function, which is dependent on the total density n and the temperature. Compared with reaction (7), we find

$$n_{H^0}^{1/2} Q^{-3/2}(H) Q(H_2^+) \frac{R(H*)}{R(H_2^+)}$$

$$= \begin{cases} 2.6 \times 10^3 , & T = 4000\ \text{K} , \\ 1.0 \times 10^5 , & T = 5000\ \text{K} , \\ 1.4 \times 10^7 , & T = 7500\ \text{K} , \\ 1.8 \times 10^8 , & T = 10,000\ \text{K} . \end{cases} \quad (16)$$

Here $Q(H_2^+)$ is the H_2^+ partition function

$$Q(H_2^+) = \sum_{n,v,J,N} g_n(N, J) \exp[-E(n, v, J, N)/kT] ,$$
$$g_n(N, J) = (2S_n + 1)(2 - \delta_{0,\Lambda_n})(2J_n + 1) \quad (17)$$

(see Sauval & Tatum 1984). For $T = 5000$ K, $Q(H_2^+) = 340.9$, and for $T = 7500$ K, $Q(H_2^+) = 1011.6$. Thus, in LTE conditions, excited atom radiative association is an important process at high temperatures and relatively low densities.

A similar result was found by an explicit calculation to be the case during the onset of the *epoch of recombination* in the early universe. At that time, the universe was approximately in thermodynamic equilibrium (TE), with a total hydrogen density of $n(H_{tot}) \sim 10^4$ cm⁻³. However, the $n = 2$ population was enhanced over the TE value as a result of resonant scattering of Lyα photons (Peebles 1968). The results from a detailed integration of molecular formation and destruction processes through the epoch of recombination are displayed in Figure 3a. For the model shown $\Omega_{tot} = 1.0$ and $\Omega_{baryon} = 0.1$ in a $H_0 = 100$ km s⁻¹ Mpc⁻¹ universe. The abundance of H_2 rises in steps, with the initial increase due, in the absence of reaction (5), to the exchange reaction of H with HeH⁺ to form H_2^+ followed by reaction (7). This process ceases to be important by redshift $z \approx 600$. Displayed in Figure 3b is the relative importance of reaction (5), which dominated the earliest formation of H_2. This period was brief and did not alter the asymp-
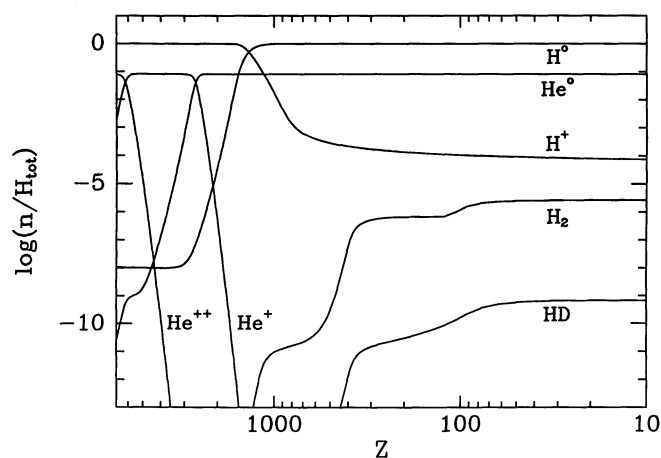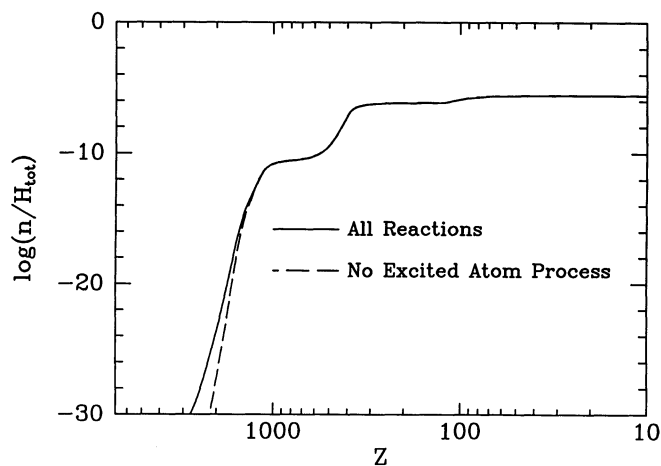
FIG. 3a

FIG. 3b

FIG. 3.—(a) Variation in atomic and molecular fractional abundances vs. redshift z around the epoch of recombination for a number of species. These are abundances by number relative to hydrogen in all forms. Elemental abundances are $H:He:D = 1.0:0.080:1.7 \times 10^{-5}$. For this model $H_0 = 100$ km s^{-1} Mpc^{-1}, $\Omega_{tot} = 1.0$, and $\Omega_{baryon} = 0.1$. The final H_2 abundance is 2.6×10^{-6}, and the final ionization fraction is $n_e/n_H = 7.8 \times 10^{-5}$. (b) Variation of molecular hydrogen abundance vs. z for the model shown in (a). This plot demonstrates the relative importance of the excited atom radiative association process to form H_2 (reaction [5]) around the epoch of recombination. The dashed curve has been calculated with reaction (5) excluded. The solid curve is the result of a calculation which included the excited atom process.

totic abundance of H_2. The next rise in H_2 abundance as seen in Figure 3a results from H_2 formation via the H_2^+ process, reactions (6) and (7). The final rise to an asymptotic abundance as $z \to 0$ is due to the H^- process, reactions (8) and (9), which becomes effective only when the radiation has become too cold to threaten H^- through photodetachment (for a much more detailed discussion see Latter 1989).

It is clear that the excited atom association process cannot compete with the other gas-phase processes in a cool diffuse cloud. However, it is of interest to note how the gas-phase processes in a "typical" diffuse cloud ($T \approx 100$ K, $n_e \approx 2 \times 10^{-4} n_H$ cm^{-3}, $n_H \approx 300$ cm^{-3}; van Dishoeck & Black 1986) compare. The required excitation temperature of $H(n = 2)$ is found to be $T_{ex} \sim 8000$ K for reaction (5) to be faster than the dominant H^- process, and $T_{ex} \sim 5400$ K for it to compete with the H_2^+ process. While this greatly exceeds the kinetic temperature of the gas, such an excitation temperature might be possible in regions of extreme Lyα trapping. For example, a diffuse H II region, such as that described by Draine & Salpeter (1978), is a Strömgren sphere surrounding an O7 V star with $n = 0.5$ cm^{-3} and $T = 8000$ K. The excitation temperature due to Lyα pumping alone is $T_{ex} \sim 3500$ K in the surrounding neutral region. Using the parameters of Black & Dishoeck (1987) for the planetary nebula NGC 7027, it can be shown that $T_{ex} \sim 5200$ K in the nebula. In this case, the density and ionization are sufficiently high that the required excitation temperature for excited atom association to be competitive is in excess of 14,000 K. At electron densities $n_e^c \gtrsim 10^4$ cm^{-3}, $2s \leftrightarrow 2p$ collisional exchange reactions with electrons and protons will bring the $2s$ population into equilibrium with the photon-pumped $2p$ state, providing a small but nonnegligible increase to the rate of reaction (5). However, at such large electron densities, the H^- process will likely be very rapid compared with reaction (5).

In a protostellar wind (e.g., Glassgold, Mamon, & Huggins 1989), the hydrogen $n = 2$ population will be elevated above thermal values by Lyα trapping and recombination. It therefore may be instructive to examine how much and when reaction (5) contributes within such an environment. Therefore, in

a detailed calculation, similar to that described by Glassgold et al. (1989), of the processes which might take place in a protostellar outflow, we have examined the contribution to H_2 formation by reaction (5). In order to determine the $n = 2$ population of neutral hydrogen we have assumed case B recombination and a thermal distribution between the $2s$ and $2p$ states. We have also included photoionization from the $n = 2$ state and collisional excitation and de-excitation. The electrons contributed by ionized metals heavier than Si were ignored. A thermal distribution was assumed for excited H_2^+ rotation-vibration levels, which enhances the destruction of H_2^+ by photodissociation at the highest gas temperatures. The wind parameters employed are identical to those used by Glassgold et al. (1989): wind velocity $V_{wind} = 150$ km s^{-1}; stellar radius $R_* = 5 \times 10^{11}$ cm; radiation temperature $T_{rad} = 5000$ K; gas temperature $T_g = T_* = 5000$ K out to a radius $R = 2R_*$; for $R > 2R_*$ the gas temperature varies as $T_g = T_*(2R_*/R)$. This fully time-dependent calculation involved 41 species composed of H, He, C, O, and Si and was comprised of 318 reactions. The solution was obtained by the Gear method (Gear 1971) and a well-tested algorithm. Elemental abundances were solar, with LTE values taken as the initial densities. The results relating to H_2 formation are shown in Figures 4 and 5. Figure 6 displays the results of a calculation where T_g was allowed to vary at the above rate starting at R_*. Because of the large ionization fraction, reaction (5) does not become competitive with the H^- process until well after H_2 has reached an asymptotic abundance, and then only for low mass-loss rates where H_2 formation is inefficient. Reaction (5) never competes with the H_2^+ process. However, Figure 6 shows that reaction (5) might need to be considered under certain conditions.

Another object in which the excited atom radiative association process might be significant in a different way is in the bipolar nebula surrounding the star HD 44179 (the Red Rectangle). The nebular spectrum of this object displays dramatic molecular band–like emission from ~ 5500 to 7500 Å (Schmidt, Cohen, & Margon 1980). These features have defied identification. It has been asserted that the emission might be
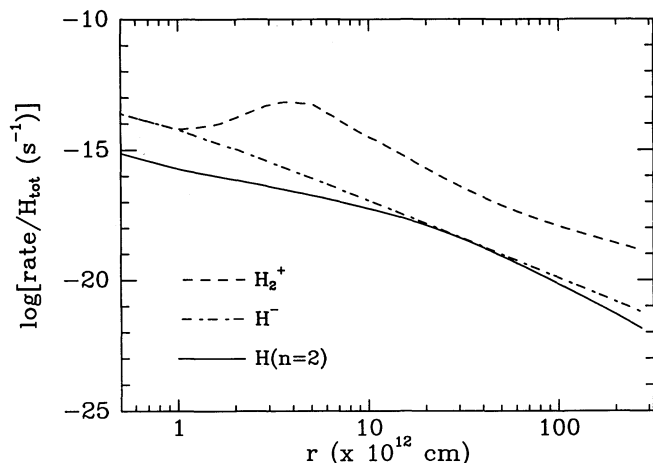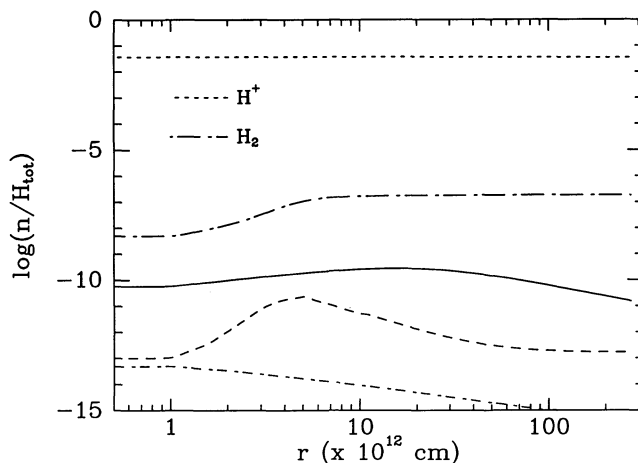
FIG. 4.—(a) Variation in rates of reactions (7) (H$_2^+$), (9) (H$^-$), and (5) [H($n = 2$)] relative to the total hydrogen density with increasing distance from the stellar surface in a protostellar wind. This wind model uses the parameters given in the text for a mass-loss rate of $\dot{M} \sim 6 \times 10^{-10}\ M_\odot\ \mathrm{yr}^{-1}$. Cooling starts at $2R_*$. (b) Variation in number density relative to the total hydrogen in all forms with increasing distance from the stellar surface. The species pictured are H$_2$ and the hydrogen species involved in the formation of H$_2$. This is the same model described in (a). The relative densities of H($n = 2$), H$^-$, and H$_2^+$ are shown with the same line types as in (a). Note that the $n = 2$ population of H increases slightly as the temperature decreases. H$_2$ formation is not very efficient in this model because of the relatively low density in the wind.

due to large molecules, or polycyclic aromatic hydrocarbons (Wdowiak 1987). Another possibility is fluorescence produced by reaction (5) occurring through the $EF\ ^1\Sigma_g^+ \rightarrow B\ ^1\Sigma_u^+$ channel. The $EF\ ^1\Sigma_g^+$ state correlates with H($2s$) and H($1s$) at large internuclear separations. While slower than the other routes already discussed ($k_{EF} \approx 2 \times 10^{-16}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ at $T = 1000$ K), it will produce an optical spectrum. Preliminary analysis shows that this process could account for at least some of the emitted flux. However, a detailed calculation of the spectrum has not yet been carried out. If Lyα trapping is responsible for the enhancement in the $n = 2$ population, then a potential diagnostic would be the presence of coexisting infrared emission from molecular hydrogen due to UV pumping of the Lyman and Werner band systems (e.g., Black & van Dishoeck 1987).

While this discussion has not been exhaustive, it should have

made apparent that situations can be envisaged where reaction (5) might play an important role. Other environments in which Lyα trapping may be significant include primordial shocks (Kang et al. 1990; Mac Low & Shull 1986) and in the gas associated closely with quasars and active galactic nuclei (Kawara, Nishida, & Gregory 1989; Krolik & Begelman 1988). At the present time, observations of molecules in these regions are difficult at best. Thus, our understanding of the physical conditions in which molecules are forming is tenuous. Until detailed studies have been carried out, and accurate observations are possible, there will remain large uncertainties in assessing the importance of this process in these hard-to-reach galaxies. As techniques improve for modeling chemical processes in rapidly evolving, high-temperature environments such as shocks or expanding winds, an application might appear closer to home. In time-dependent situations, the $n = 2$
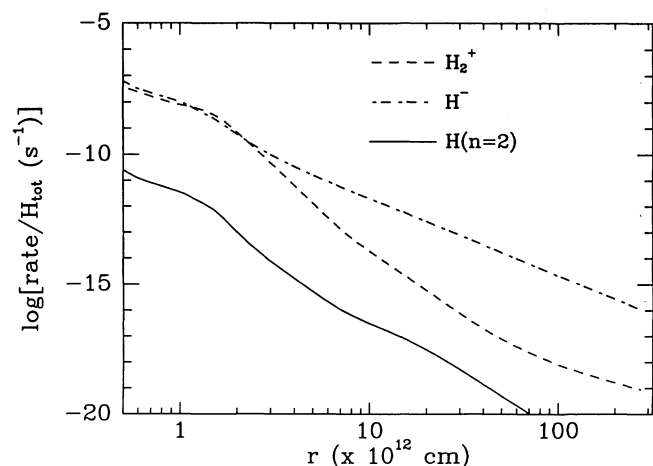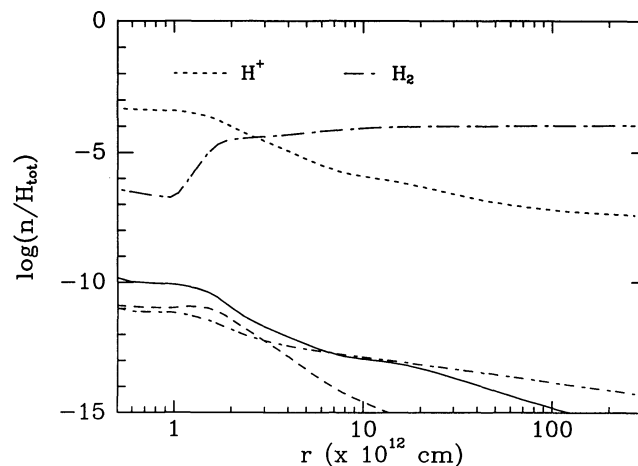

FIG. 5.—(a) As in Fig. 4a, but for a higher mass-loss rate ($\dot{M} \sim 6 \times 10^{-6}\ M_\odot\ \mathrm{yr}^{-1}$). Note that the excited atom process is relatively much less efficient in this higher density model. (b) As in Fig. 4b, but for the higher mass-loss rate model pictured in (a). Notice the much more efficient formation of H$_2$ at the higher density. The $n = 2$ population of H decreases with temperature in this model because of the much slower rate of recombination at later times.
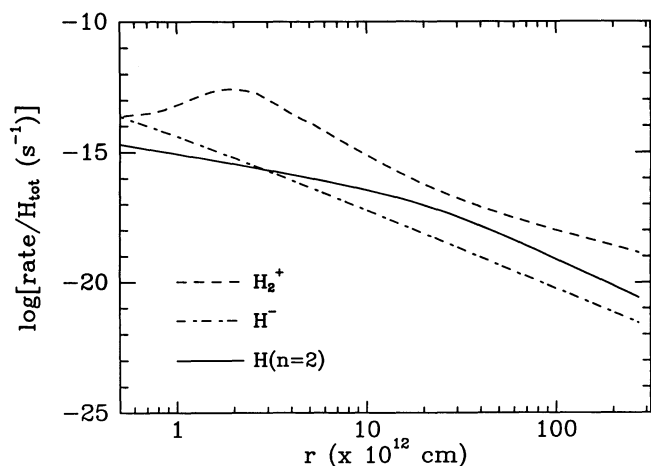
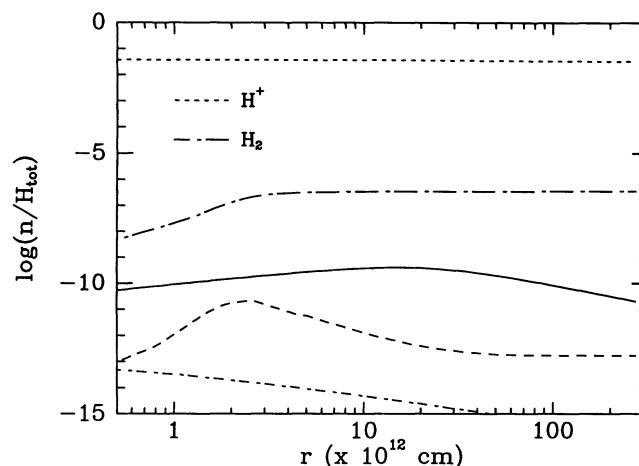FIG. 6a   FIG. 6b

FIG. 6.—(a) Same model as pictured in Fig. 4, only here cooling was allowed to begin at the stellar surface. Note the increased importance of reaction (5) at later times. (b) Variation in number density relative to total hydrogen for the model pictured in (a). Note that the asymptotic H_2 abundance is only slightly higher than that found for the model pictured in Fig. 4b. The enhanced effectiveness of reaction (5) in this model occurs only after the H_2 abundance has reached a maximum value. Therefore, the addition of reaction (5) does not alter the final result.

population could be elevated for a brief period, resulting in a burst of molecular hydrogen formation. Important transient effects might ensue. Indeed, it may prove to be true that the conditions in the universe always conspire in ways which make reaction (5) unimportant. This somehow seems unlikely.

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