Ch/Ge 128 - Cosmochemistry

The Primordial Bond -
H_2 in Diffuse Clouds

We start with an assumption — that H_2 is the primordial molecule and the H-H bond is the primordial bond.

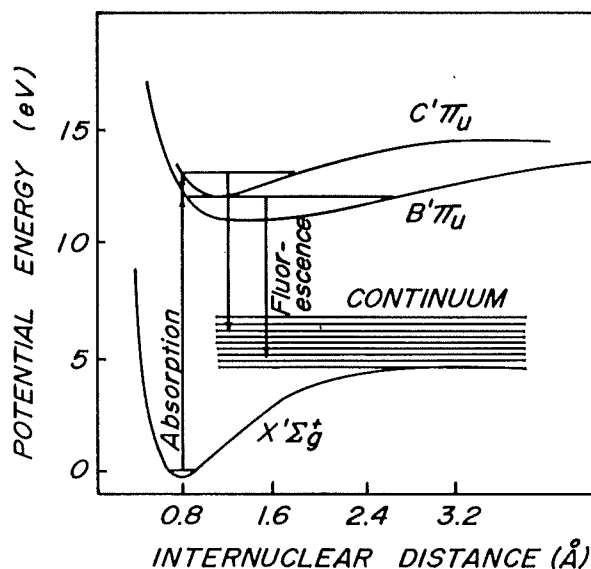We will be required to prove this assumption at some point. The rationale for the assumption is:

- H atoms are by far the most abundant in the universe.

- H_2 is the simplest molecule.

- Observations show H_2 is abundant in diffuse clouds.

Now we need a mechanism; but first we need to determine the required formation rate. To do this we will find the loss rate, then require formation to balance the loss.
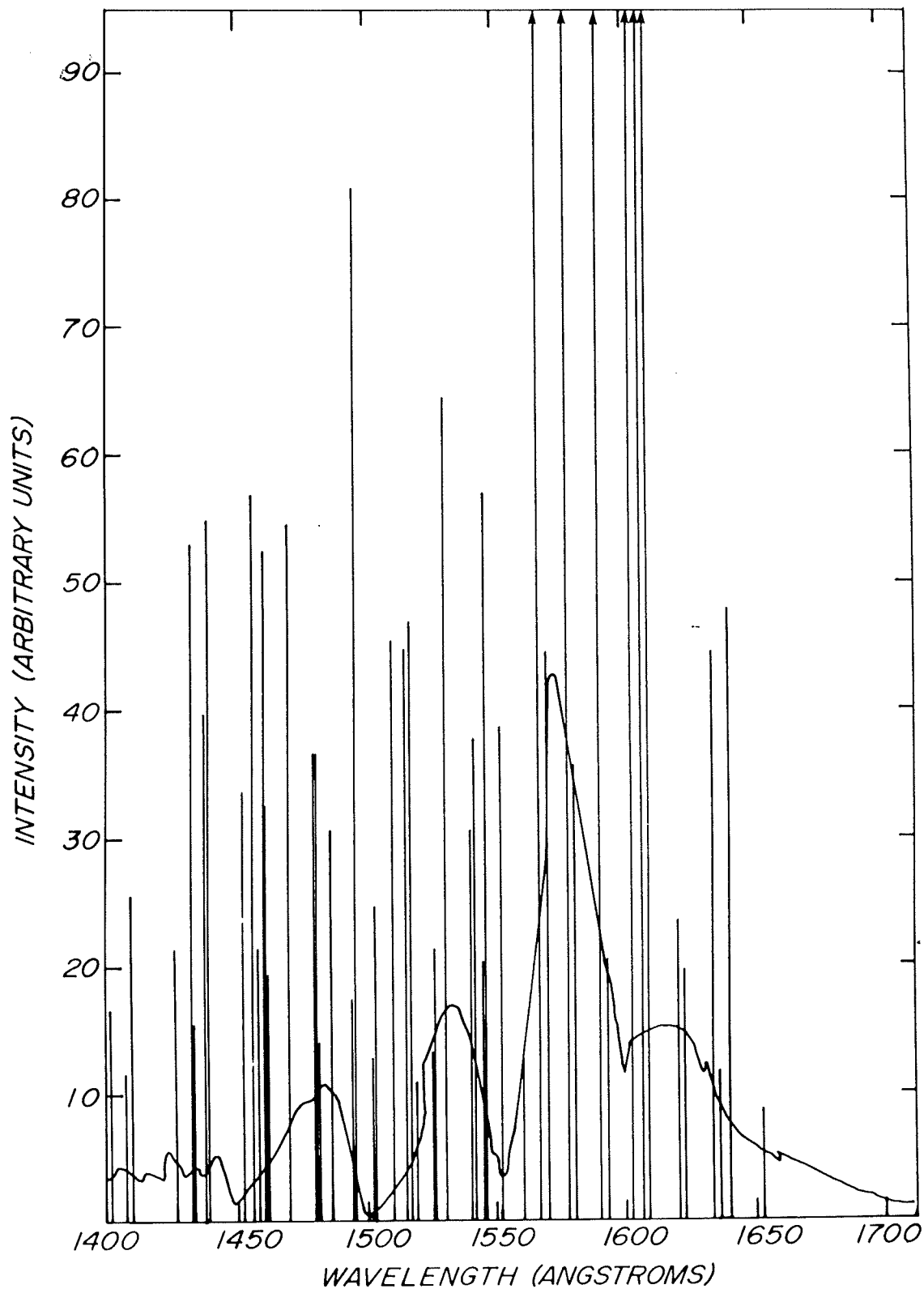
We will also make the second assumption that the major loss process for H_2 is photodissociation, and will later show this to be true.

A simplified energy level diagram for H_2 looks like:

{ see Ch. 6, Duley & Williams }

There are no allowed transitions to repulsive states from the ground state at energies less than the Lyman limit (13.595 eV).

However, there are transitions to excited levels

$$H_2(X\,^1\Sigma_g^+, v=0) + h\nu \longrightarrow H_2(B\,^1\Sigma_u^+, v') \quad \lambda < 1109\,\overset{\circ}{A}$$
$$\longrightarrow H_2(C\,^1\Pi_u, v') \quad \lambda < 1009\,\overset{\circ}{A}$$

at energies < 13.6 eV, followed by fluorescence back to excited levels of the ground state and to repulsive continuum levels of the ground state:

$$H_2(B\,^1\Sigma_u^+, v') \longrightarrow H_2(X\,^1\Sigma_g^+, v'') + h\nu$$
$$\longrightarrow H + H + h\nu$$

$$H_2(C\,^1\Pi_u, v') \longrightarrow H_2(X\,^1\Sigma_g^+, v'') + h\nu$$
$$\longrightarrow H + H + h\nu$$

From quantum mechanical calculations, the fraction leading to dissociation is

$$f_D(X \to B) \cong 0.23$$

$$f_D(X \to C) \cong 0.01$$

The relative strength of fluorescent emission in non-dissociative vs. dissociative processes is illustrated on the following page.

Fig. 6.6 Relative emission spectrum in the Lyman bands (sharp lines), and continuum in the wavelength range $0.14 \leq \lambda \leq 0.17\ \mu m$, in the fluorescence spectrum of hydrogen. (W. W. Duley and D. A. Williams, *Astrophysical Journal*, Letters, 1980, **242**, L179.)

One must now calculate the dissociation rate using the interstellar radiation field and the cross sections for H_2 photodissociation:

$$\Gamma_{H_2} = \int_{912\text{\AA}}^{\infty} \sigma_D(\lambda)\, F(\lambda)\, d\lambda \quad .$$

The interstellar radiation field has the form
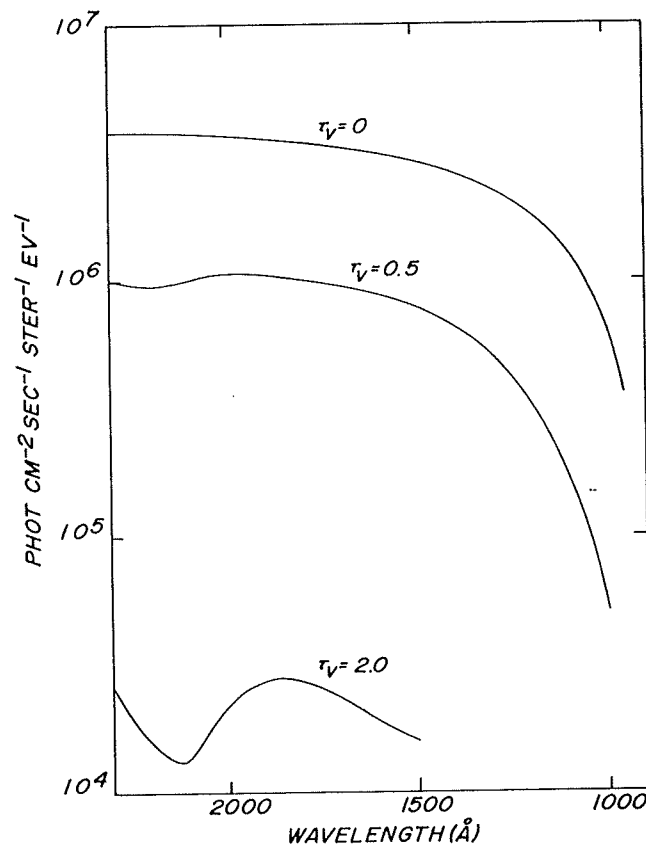
Fig. 4.4 The interstellar radiation flux $F(E)$ photons $\text{cm}^{-2}\text{s}^{-1}\text{eV}^{-1}\text{ster}^{-1}$ in unobscured regions of the interstellar medium, in a typical diffuse cloud with $\tau_v \approx 0.5$, and in a denser cloud with $\tau_v \approx 2$.

The cross section calculated is then

$$\Gamma_{H_2} = 5.2 \times 10^{-11}\ s^{-1}$$

in the unattenuated interstellar radiation field.

Ch. 4 of Duley & Williams outlines similar calculations dealing with the photophysics and photochemistry of a variety of interstellar species.

Further, the H_2 molecule has the interesting property in the ISM that it is efficient at _self-shielding_:

Since photodissociation occurs via a line spectrum (albiet broad), once these photons are absorbed, the molecule can no longer be photodissociated. The figure below shows the self-shielding effect for photodissociation & fluorescence in H_2.
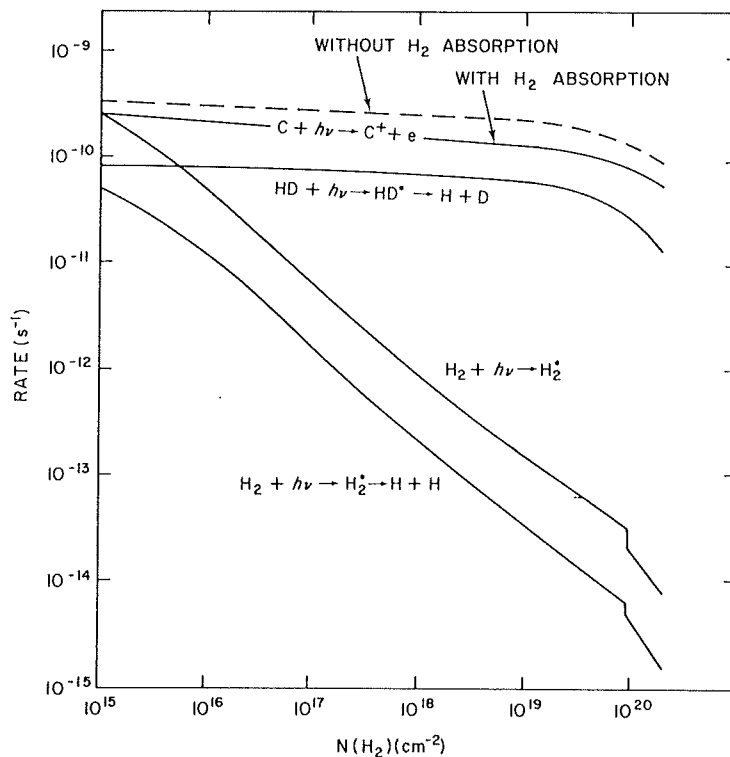
Fig. 4.7 Dependence of β on $N(H_2)$ (H_2 column density) for H_2 and HD. Note that $\beta(HD)$ is not reduced by self-shielding. The effect of H_2 absorption on the photoionization rate of C is also shown. (J. H. Black and A. Dalgarno, *Astrophysical Journal Supplement Series*, 1977, **34**, 405.)

Simply put, this means that H_2 can effectively _protect_ itself in clouds with sufficient column density.

A cloud of radius $1 pc = 3 \times 10^{18}$ cm and a density of 100 cm^{-3} has a column density of

$$N = 3 \times 10^{20} \quad cm^{-2}$$

and is effectively self-shielded.

Assuming a uniform distribution along the line of sight:

Table 6.1 Column densities $N(H)$ and $N(H_2)$ for several paths through the interstellar medium; $\langle n \rangle = n(H) + 2n(H_2)$ is the total space density of H, assuming a uniform distribution along the entire line of sight, r; τ_v is the total visual extinction due to dust over the path r.

Star	r (pc)*	τ_v	$N(H)$ (cm^{-2})	$N(H_2)$ (cm^{-2})	$\langle n \rangle$ (cm^{-3})	f
λSco	102	0.08	2.4×10^{19}	5.0×10^{12}	0.076	4.2×10^{-7}
ζPup	668	0.14	1.0×10^{20}	2.8×10^{14}	0.047	6.0×10^{-6}
τSco	236	0.165	3.1×10^{20}	3.2×10^{14}	0.42	2.0×10^{-6}
ξOri	409	0.22	2.8×10^{20}	3.7×10^{16}	0.22	2.6×10^{-4}
10 Lac	589	0.30	5.0×10^{20}	1.6×10^{19}	0.29	6.0×10^{-2}
ξPer	538	0.91	1.3×10^{21}	3.4×10^{20}	1.2	3.5×10^{-1}
ζPer	394	0.91	6.5×10^{20}	4.7×10^{20}	1.3	5.9×10^{-1}
ζOph	138	0.88	5.2×10^{20}	4.5×10^{20}	3.3	6.3×10^{-1}

column densities of H and H_2, $N(H)$ and $N(H_2)$, show the rapid transition from atomic to molecular hydrogen as τ increases. In this table

$$ f = \int \frac{2n(H_2)}{n(H) + 2n(H_2)} \cong \frac{2N(H_2)}{N(H) + 2N(H_2)} $$

We now use the maximum calculated loss rate to derive the most stringent requirement on the formation rate on grains:

$$ \frac{d}{dt} n(H_2) = k_g n_g \, n(H) n(H) - \Gamma_{H_2} \, n(H_2) = 0 $$

in steady state.

$$ \therefore \quad k_g n_g \, n(H) n(H) = \Gamma_{H_2} \, n(H_2) $$

The rate of formation of H_2 is $k_g n_g n(H) \ s^{-1}$, and the effective rate constant is $k_g n_g = R \ cm^3 s^{-1}$

$$ \Rightarrow \quad R \, n(H) n(H) = \Gamma \, n(H_2) $$

and for a diffuse cloud where

$$ f = \frac{2n(H_2)}{2n(H_2) + n(H)} << 1 $$

$$ \Rightarrow \quad R = \frac{\Gamma f}{2n} $$

For some "typical"

lines-of-sight ⟹

Star	n (cm^{-3})	Γ_{0} (s^{-1})	f	R (cm^3 s^{-1})
δOri	10–30	5.5×10^{-11}	5.6×10^{-6}	1.5×10^{-17} to 5.2×10^{-18}
τSco	10–100	4.4×10^{-10}	2.0×10^{-6}	4.4×10^{-17} to 4.4×10^{-18}
ζPup	100	1.8×10^{-9}	6.0×10^{-6}	5.3×10^{-17}

The canonical value is usually taken to be

$$R = 3 \times 10^{-17} \ \text{cm}^3 \text{s}^{-1}.$$

How does this stack up against grain formation?

Molecule formation on grains

There are several steps (here for H_2):

1. An H atom must collide with a grain.

2. The colliding atom must be accomodated (adsorbed).

3. The H atom must be retained until another H atom is absorbed.

4. The H atoms must be mobile in order to find each other.

5. H_2 must be formed in the collision and ejected from the surface.

1. The formation rate for H_2 on grains is

$$k_c \, P n_g \, n(H) = \langle \pi a^2 n_g \rangle_n \, v_H \, P n(H) \qquad s^{-1}$$

$$ = 3 \times 10^{-22} \, n \, v_H \, P n(H)$$

$$ = 3 \times 10^{-17} \, P \, n \cdot n(H)$$

for $v_H = 1 \times 10^5$ cm/s

The "effective two body" rate constant is $k_c P n_g$ cm^{3}s^{-1}

or

$$k^{(2)} = 3 \times 10^{-17} \, P n \quad cm^3 s^{-1},$$

and to meet the required ("observed") $R = 3 \times 10^{-17}$ cm^{3}s^{-1}

we need the product Pn to be large.

2. To determine the absorption times, use a classical expression;

$$t_a = \frac{1}{\nu} e^{D/kT}$$

which says that the probability for overcoming a barrier of height D at a temperature T is $\sim e^{-D/kT}$, and that there are ν opportunities/second to overcome the barrier.

ν is the vibrational frequency for H in the absorption potential. For a particle-in-a-box potential

$$\nu \cong D/h \approx 10^{12} \, s^{-1}.$$

If the H is physi-sorbed we take

$$D_p \sim 400 \, K \quad,$$

and if chemi-sorbed we use, as an extreme value,

$$D_c \lesssim 2eV = 20,000 \, K.$$

Thus,

$$\begin{array}{lll} t_a \cong 3 \times 10^5 \, s & @ \, 10K & \left. \right\} \begin{array}{l} \text{physical} \\ \text{absorption} \end{array} \\ " \cong 2 \times 10^{-8} \, s & @ \, 40K & \\ t_a = \infty & @ \, 100K & \text{chemisorption} \end{array}$$

$\Rightarrow$ H atoms will evaporate above 40K (perhaps less) before forming H_2, unless there are strong binding sites!

3.   The time between collisions of H-atoms & grains is

$$t_c = \frac{1}{k_c\, n(H)} = \frac{1}{\pi a^2 v_H\, n(H)} = \frac{1}{\pi\, (10^{-5}\,cm)^2\,(10^5\,cm/s)\, n(H)}$$

or

$$t_c = 3\times10^4 \; s \qquad \text{for} \quad n(H) = 1$$

$$t_c = 300 \;\; s \qquad \text{for} \quad n(H) = 100$$

∴ At low T, physical absorption will retain H atoms long enough, but chemisorption is required at "high" T. The breakpoint is about $T \sim 15 K$.

4.   If we postulate that chemisorption sites are present to accomodate H_2 formation at higher temperature, the H atoms must be able to find them. <u>Note</u>: The H atoms are <u>not</u> mobile if at a chemisorption site. What is the physisorption mobility?

Use the standard quantum solution for barrier penetration:
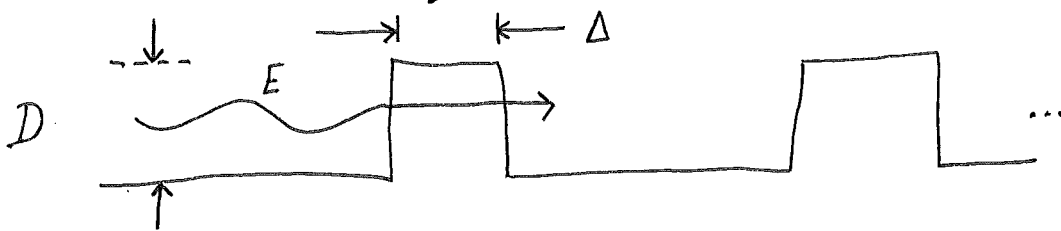
$$P = 1 + \left[\frac{D^2 \sinh^2 \beta\Delta}{4E\,(D-E)} \right]^{-1} \qquad \beta = \sqrt{2m\,(D-E)\,\hbar^2}$$

For $D = 400\,K$, $E = h\nu$ w/$\nu = 10^{12}\,s^{-1}$, $m = m_H$ & $\Delta = 1\,\text{Å}$

$$P = 10^{-3} \quad,$$

and the time required to penetrate the barrier is

$$t_h = \frac{1}{p_\nu} = 10^{-9} \text{ s} \qquad \text{``hopping'' time}$$

for an individual hop. Thus, H atoms are <u>very</u> mobile if held by physical adsorption.

The time to find another site on the grain, for a random, 2D walk, is:

$$t_m = \lambda^2 t_h \qquad \lambda = \# \text{ of ``hops'' needed}$$

Assume, as a worst case, there is only one chemisorption site on a $0.1 \mu m$ grain

$$\Rightarrow \quad \lambda = \frac{(\pi d/2)}{r} \qquad \left\{ \frac{\text{distance between sites}}{\text{spacing of sites}} \right\}$$

If $d = 1 \times 10^{-5}$ cm and $r = 1.5 \text{ Å} = 1.5 \times 10^{-8}$ cm

$$\Rightarrow \quad \lambda \cong 10^3 \quad \& \quad t_m = \lambda^2 t_h = 10^{-3} \text{ s}$$

$\therefore$ $t_m \ll t_c$, so that the H atom can find the chemisorption site before the next collision.

<u>and</u> $\qquad t_m \sim t_a \qquad$ for $T \lesssim 20K$

so when $T \lesssim 20K$ the H-atom can find the chemisorption site(s) before evaporating.

To be able to raise the temperature for H_2 formation on grains, we need increasing #'s of chemisorption sites. We postulate that the grains have large #'s of chemisorption sites so that H_2 can be formed at $T \cong 100K$.

The consequence is that a grain is saturated with H atoms _and_ the rate of formation of H_2 is controlled by the rate of arrival of H atoms at the surface.

5. Assume H_2 is formed out of _every_ H-H encounter.

In essence, trade a grain-H chemical bond for an H-H molecular bond. There are now no strong grain-H_2 bonds, the H_2 can only be physically adsorbed, and

$$t_{evaporation} \cong \nu_{H_2}^{-1} \, e^{D_{H_2}/kT} \leq t_a(H).$$

Under these conditions, $P \cong 1$ and

$$k_g \cong 3 \times 10^{-17} \, n \qquad cm^3 s^{-1}$$

which is just what is observed in the diffuse ISM!

<u>What about the gas phase?</u>

1. The simplest way is just to stick two H-atoms together:

$$H + H \longrightarrow H_2 + h\nu$$

<u>Problem:</u>

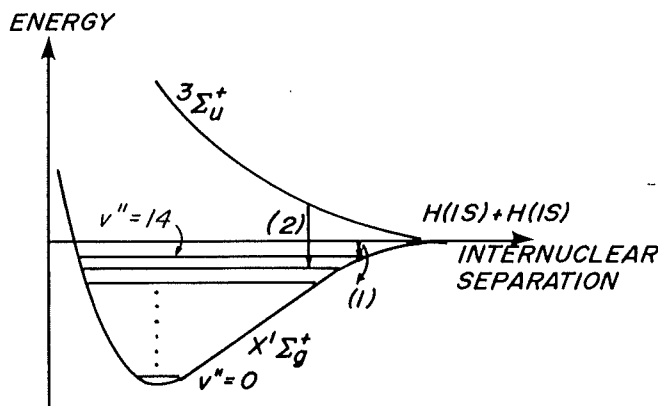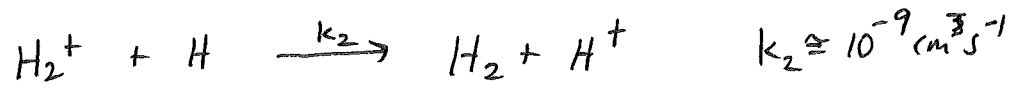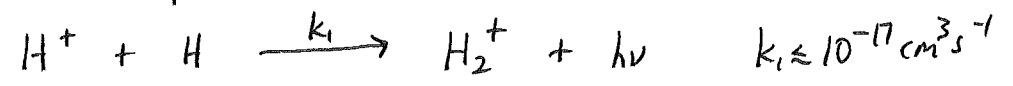There are _no_ low-lying states that are available in the H_2 molecule.

Fig. 6.4 Potential energy curves for two ground state H atoms. $X^1\Sigma_g^+$ is the normal ground state of H_2. Stabilizing collisions that lead to radiative association are shown. (1) is a transition between $v'' =$ continuum and $v'' = 14$ of the $X^1\Sigma_g^+$ state. (2) is a spin forbidden $^3\Sigma_g^+ \rightarrow X^1\Sigma_g^+$ electronic transition.

You could try $^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ at large separations[1] or emission from the continuum to high lying vibrational states [(2) in figure], but both are _very_ slow.   Essentially will not work...
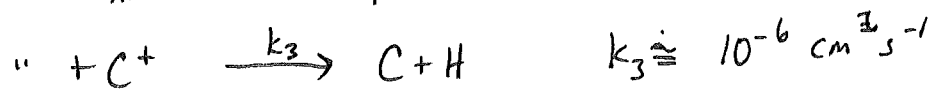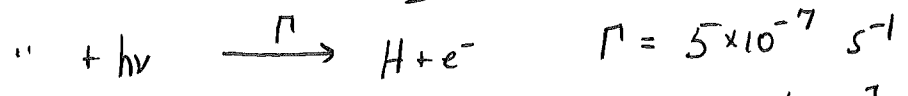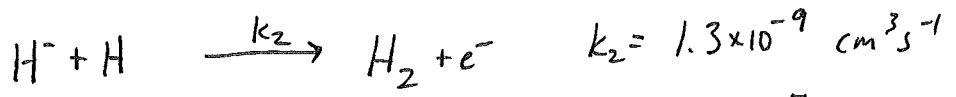
2.   Try it with a proton:

$$H^+ + H \xrightarrow{k_1} H_2^+ + h\nu \qquad k_1 \lesssim 10^{-17} cm^3 s^{-1}$$

$$H_2^+ + H \xrightarrow{k_2} H_2 + H^+ \qquad k_2 \cong 10^{-9} cm^3 s^{-1}$$

$$R = k_2 n(H_2^+) \qquad\qquad n(H_2^+) = \frac{k_1 n(H^+) n(H)}{k_2 n(H)}$$

$$0\% \qquad k_2 n(H_2^+) = k_1 n(H^+)$$
$$\text{"} \qquad \leq 10^{-17} n(H^+)$$

Further, $n(H^+) \ll n(H)$ and $k_g = 10^{-17} n(H)$!

3.   Try it with a negative ion:

$$H + e^- \xrightarrow{k_1} H^- \qquad k_1 = 10^{-18} T \ \ cm^3 s^{-1}$$

$$H^- + H \xrightarrow{k_2} H_2 + e^- \qquad k_2 = 1.3 \times 10^{-9} \ cm^3 s^{-1}$$

$$\text{"} + h\nu \xrightarrow{\Gamma} H + e^- \qquad \Gamma = 5 \times 10^{-7} \ s^{-1}$$

$$\text{"} + C^+ \xrightarrow{k_3} C + H \qquad k_3 \cong 10^{-6} \ cm^3 s^{-1}$$

We want $k_2 n(H^-)$;

use steady state

$$\Longrightarrow \quad n(H^-) = \frac{k_1 n(H) n(e^-)}{k_2 n(H) + k_3 n(C^+) + \Gamma}$$

What is the fatest loss process?

$$\frac{k_2\, n(H)}{\Gamma} = \frac{1.3\times10^{-9}\, n(H)}{5\times10^{-7}} = 3\times10^{-3}\, n(H)$$

so for $n \lesssim 300$, photodetachment wins.

$$\frac{k_3\, n(C^+)}{\Gamma} = \frac{10^{-6}\cdot 10^{-4}\, n(H)}{5\times10^{-7}} = 2\times10^{-4}\, n(H)$$

so photodetachment wins again.

0% $$k_2\, n(H^-) = \frac{k_1\, k_2\, n(e^-)\, n(H)}{\Gamma}$$

$$" = \frac{(10^{-18}T)(1.3\times10^{-9})\left[10^{-4} n(H)\right] n(H)}{5\times10^{-7}}$$

$$" = 3\times10^{-25} n^2\, T$$

For $n \lesssim 100$ and $T = 100$, $k_2\, n(H^-) = 10^{-20}$ cm^3 s^{-1}

$$\ll k_g$$

0% Grain synthesis of H_2 "wins"

But recall that the process has to be nearly "perfect"!

Note: In the early universe, there are no grains. There is also no C^+ & less visible/UV radiation. Mechanism #3 above therefore becomes quite important to the chemistry of the early universe & the first generation of star formation.