COMPARING GAS-PHASE AND GRAIN-CATALYZED H_2 FORMATION

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ABSTRACT

Because H_2 formation on dust-grain surfaces completely dominates gas-phase H_2 formation in local molecular clouds, it is often assumed that gas-phase formation is never important. In fact, it is the dominant mechanism in a number of cases. In this paper, I briefly summarize the chemistry of gas-phase H_2 formation and show that it dominates for dust-to-gas ratios less than a critical value D_{cr}. I also show that D_{cr} is simple to calculate for any given astrophysical situation and illustrate this with a number of examples, ranging from H_2 formation in warm atomic gas in the Milky Way to the formation of protogalaxies at high redshift.

Subject headings: astrochemistry — ISM: molecules — molecular processes

1. INTRODUCTION

In local molecular clouds, molecular hydrogen (H_2) forms primarily on the surface of dust grains: two hydrogen atoms are adsorbed onto the surface of the grain and react to form H_2, which subsequently escapes back into the interstellar medium (ISM). However, H_2 can also form in the gas phase, primarily through the reactions

$$H + e \rightarrow H^- + \gamma \, , \tag{1}$$

$$H^- + H \rightarrow H_2 + e \, , \tag{2}$$
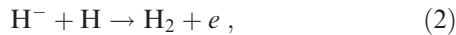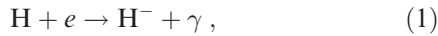
although some also forms via the slower reactions

$$H + H^+ \rightarrow H_2^+ + \gamma \, , \tag{3}$$

$$H_2^+ + H \rightarrow H_2 + H^+ \, . \tag{4}$$
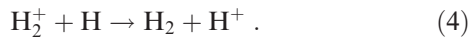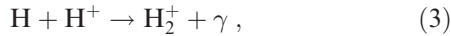
In dense gas, three-body reactions can also be important (Palla, Salpeter, & Stahler 1983), but these are ineffective at number densities $n < 10^8 \ \mathrm{cm}^{-3}$.

Discussions of H_2 formation have tended to concentrate on the role played by dust, with little attention given to the gas-phase reactions. However, as I show in § 4, in some circumstances these reactions can dominate the H_2 formation rate.

In this paper I briefly outline the chemistry of H_2 formation and show that it is easy to identify a critical dust-to-gas ratio D_{cr}, above which grain-catalyzed formation dominates. I illustrate the method by applying it to various situations of astrophysical interest and show that it can be a useful tool for estimating the importance of gas-phase H_2 formation.

2. THE FORMATION OF MOLECULAR HYDROGEN

2.1. *Gas-Phase Formation*

Most of the molecular hydrogen that forms in the gas phase does so via the formation of an intermediate H^- ion, as outlined in reactions (1) and (2) above. The first of these reactions occurs much more slowly than the second, and so the equilibrium abundance of H^- is small and is rapidly reached. Thereafter, the H_2 formation rate is determined by two factors: the rate at which H^- forms and the fraction of H^- ions that survive to form H_2. The latter quantity is

determined by competition between H_2 formation via reaction (2) and H^- destruction by mutual neutralization with H^+ ions,

$$H^- + H^+ \rightarrow 2H \, , \tag{5}$$

and by photodetachment by the incident radiation field,

$$H^- + \gamma \rightarrow H + e \, . \tag{6}$$

Various other reactions also destroy H^-, but these either are significantly slower than those above or become important only at high temperatures, in which case any H_2 that does form is very quickly collisionally dissociated. For more details, the reader is referred to the recent reviews of Abel et al. (1997), Galli & Palla (1998), Stancil, Lepp, & Dalgarno (1998), and Lepp, Stancil, & Dalgarno (2002).

If we assume, for simplicity, that H^- has already reached its equilibrium abundance, then we can write the H_2 formation rate as

$$R_{H_2,H^-} = k_1 n_e n_H \frac{k_2 n_H}{k_2 n_H + k_5 n_{H^+} + k_6} \, , \tag{7}$$

where n_i is the number density of species i and where the rate coefficients k_i for the various reactions are listed in Table 1.

If H_2 formation via reaction (2) occurs much faster than the destruction of H^- by the other reactions, then this reduces to

$$R_{H_2,H^-} \simeq k_1 n_e n_H \, ; \tag{8}$$

in other words, the H_2 formation rate is approximately the same as the H^- formation rate.

If, on the other hand, mutual neutralization dominates over H_2 formation or photodetachment as a means of removing H^-, then equation (7) becomes

$$R_{H_2,H^-} \simeq k_1 n_e n_H \frac{k_2}{k_5 x} \, , \tag{9}$$

where $x = n_{H^+}/n_H$ is the fractional ionization of hydrogen. As long as $n_e \simeq n_{H^+}$, this equation can be further simplified to

$$R_{H_2,H^-} \simeq \frac{k_1 k_2}{k_5} n_H^2 \, . \tag{10}$$

Reaction	Rate $(\text{cm}^{-3}\,\text{s}^{-1})$	Reference
$H + e \rightarrow H^- + \gamma$	$k_1 = 1.4 \times 10^{-18} T^{0.928} \exp\left(-\dfrac{T}{16200}\right)$	1
$H^- + H \rightarrow H_2 + e$	$k_2 = \begin{cases} 1.5 \times 10^{-9}, & T < 300\ \text{K}, \\ 4.0 \times 10^{-9} T^{-0.17}, & T > 300\ \text{K} \end{cases}$	2
$H + H^+ \rightarrow H_2^+ + \gamma$	$k_3 = \text{dex}[-19.38 - 1.523 \log T + 1.118 \log(T)^2 - 0.1269 \log(T)^3]$	3
$H_2^+ + H \rightarrow H_2 + H^+$	$k_4 = 6.4 \times 10^{-10}$	4
$H^- + H^+ \rightarrow 2H$	$k_5 = 5.7 \times 10^{-6} T^{-0.5} + 6.3 \times 10^{-8} - 9.2 \times 10^{-11} T^{0.5} + 4.4 \times 10^{-13} T$	5
$H^- + \gamma \rightarrow H + e$	See text	...
$H_2^+ + e \rightarrow 2H$	$k_7 = \begin{cases} 1.0 \times 10^{-8}, & T < 617\ \text{K}, \\ 1.32 \times 10^{-6} T^{-0.76}, & T > 617\ \text{K} \end{cases}$	6
$H_2^+ + \gamma \rightarrow H + H^+$	See text	...
$H + H + \text{grain} \rightarrow H_2 + \text{grain}$	See text	...

REFERENCES.—(1) de Jong 1972; (2) Launay, Le Dourneuf, & Zeippen 1991; (3) Ramaker & Peek 1976; (4) Karpas, Anicich, & Huntress 1979; (5) Moseley et al. 1970; (6) Schneider et al. 1994.

Comparing this equation with equation (8), we see that for a small fractional ionization, $R_{H_2} \propto x$, but that once the fractional ionization becomes large enough that mutual neutralization dominates, R_{H_2} becomes independent of the ionization: although increases in x still increase the H^- formation rate, this is balanced by the increase in the mutual neutralization rate and consequent decrease in the fraction of H^- ions surviving to form H_2. This change in behavior occurs for fractional ionizations near a critical value x_{cr}, defined by

$$x_{cr} = \frac{k_2}{k_5}. \qquad (11)$$

The precise value of x_{cr} is somewhat uncertain because of the significant uncertainty that remains in the determination of the mutual neutralization rate. In this paper I have chosen to adopt the rate listed in Galli & Palla (1998), which is derived from the data of Moseley, Aberth, & Peterson (1970). This is a conservative choice, in that it gives the lowest value of x_{cr}; other possibilities include the rates of Duley & Williams (1984), Dalgarno & Lepp (1987), and Croft, Dickinson, & Gadéa (1999), with the latter being preferred by the most recent compilation (Lepp et al. 2002). For the temperature range of interest, the Galli & Palla rate gives us a value $x_{cr} \sim 5 \times 10^{-3}$, with only a slight dependence on temperature. The alternative rates typically give values of x_{cr} that are factors of a few larger.

When the destruction rate of H^- ions is dominated by photodetachment, we obtain another limiting case of equation (7):

$$R_{H_2,H^-} \simeq k_1 n_e n_H \frac{k_2 n_H}{k_6}. \qquad (12)$$

This can be written as the H^- formation rate divided by a suppression factor f_{rad}:

$$R_{H_2,H^-} \simeq \frac{k_1 n_e n_H}{f_{rad}}, \qquad (13)$$

where

$$f_{rad} = \frac{k_6}{k_2 n_H}. \qquad (14)$$

Determination of the photodetachment rate, and hence f_{rad}, requires knowledge of the incident radiation field. Provided that the opacity of the gas is low, we can write the photodetachment rate as

$$k_6 = 4\pi \int_{\nu_{th}}^{\infty} \frac{\sigma_\nu J_\nu}{h\nu}\, d\nu, \qquad (15)$$

where J_ν is the mean specific intensity, σ_ν is the photodetachment cross section (de Jong 1972),

$$\sigma_\nu = 7.928 \times 10^5 \frac{(\nu - \nu_{th})^{3/2}}{\nu^3}\ \text{cm}^{-2}, \qquad (16)$$

and $h\nu_{th} = 0.755$ eV is the energy threshold for H^- photodetachment.

Evaluating equation (15) for the local interstellar radiation field, as estimated by Mathis, Mezger, & Panagia (1983), gives

$$k_6 = 4.2 \times 10^{-7}\ \text{s}^{-1}, \qquad (17)$$

and so locally,

$$f_{rad} = 3.2 \times 10^2 n_H^{-1}. \qquad (18)$$

If the opacity of the gas is high, then this will overestimate the effects of radiation. However, at frequencies near the H^- photodetachment threshold, the continuum opacity of interstellar gas is low and absorption is dominated by dust. Consequently, a high opacity implies a high dust content, in which case grain-catalyzed formation will dominate.

These limiting cases provide useful insight into the physics of gas-phase H_2 formation, but in general we must use the full form of equation (7), which we can rewrite as
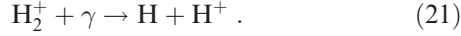
$$R_{H_2,H^-} = \frac{k_1 n_e n_H}{1 + x/x_{cr} + f_{rad}}. \qquad (19)$$

If we now turn to H_2 formation via the H_2^+ ion, we find that the basic chemistry is remarkably similar. H_2^+ is created by the radiative association of H and H^+ (reaction [3]) and destroyed by H_2 formation (reaction [4]), dissociative

recombination,

$$H_2^+ + e \rightarrow 2H , \qquad (20)$$

and photodissociation,

$$H_2^+ + \gamma \rightarrow H + H^+ . \qquad (21)$$

As with H$^-$, the formation of the molecular ion is the limiting step, with subsequent reactions occurring orders of magnitude faster. If we again assume that the H$_2^+$ abundance has reached equilibrium, then we can write the H$_2$ formation rate as

$$R_{H_2,H_2^+} = k_3 n_{H^+} n_H \frac{k_4 n_H}{k_4 n_H + k_7 n_e + k_8} , \qquad (22)$$

which has the same form as equation (7). Indeed, we can rewrite it as

$$R_{H_2,H_2^+} = \frac{k_3 n_{H^+} n_H}{1 + x/x_{cr} + f_{rad}} , \qquad (23)$$

only now

$$x_{cr} = \frac{k_4}{k_7} , \qquad (24)$$

and,

$$f_{rad} = \frac{k_8}{k_4 n_H} , \qquad (25)$$

where the photodissociation rate k_8 is calculated in a similar fashion to the photodetachment rate above. Evaluating these, we find that x_{cr} for H$_2^+$ is typically an order of magnitude larger than for H$^-$ and that in the local ISM,

$$f_{rad} \simeq n_H^{-1} , \qquad (26)$$

where I have again used the Mathis et al. (1983) radiation field, together with the H$_2^+$ photodissociation cross section from Shapiro & Kang (1987).

Comparing these values with those for H$^-$, we see that H$_2^+$ is significantly more robust. However, it forms at a much slower rate (between 2 and 3 orders of magnitude, depending on temperature), and so in most cases H$^-$ dominates. Nevertheless, there are exceptions, as we see in § 4.

Finally, a few other possible mechanisms have been suggested for gas-phase H$_2$ formation. Latter & Black (1991) propose that H$_2$ can form as a result of direct radiative association,

$$H + H \rightarrow H_2 + \gamma , \qquad (27)$$

provided that one of the hydrogen atoms is in an excited electronic state. Rawlings, Drew, & Barlow (1993) show that a more efficient mechanism is formation of H$_2^+$ by associative ionization,

$$H + H \rightarrow H_2^+ + e , \qquad (28)$$
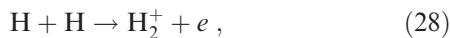
with the H$_2^+$ thereafter forming H$_2$ by reaction (4) above. This mechanism again requires one of the hydrogen atoms to be in an excited atomic state. However, this requirement means that in general these reactions are not important, since the necessary population of excited atomic hydrogen is only found in a few unusual circumstances, such as in the universe immediately after recombination.

2.2. Grain-catalyzed H$_2$ Formation

Despite its importance in local interstellar chemistry, the rate of H$_2$ formation on dust grains is still uncertain. In local molecular clouds, observations suggest a formation rate (Jura 1975)

$$k_9 \sim 3 \times 10^{-17} \ \mathrm{cm^3 \ s^{-1}} . \qquad (29)$$

Observations of H$_2$ in the LMC and SMC with the *Far Ultraviolet Spectroscopic Explorer* (*FUSE*) satellite (Tumlinson et al. 2002) suggest a value that is an order of magnitude smaller, but this is consistent with the underlying rate per unit dust mass being the same, since the mean dust-to-gas ratio within these galaxies is significantly smaller than in the Milky Way (Issa, MacLaren, & Wolfendale 1990).

Unfortunately, direct measurements of this kind can only give us information about H$_2$ formation in physical conditions that are easily accessible to observations and provide little basis on which to predict the H$_2$ formation rate in different regimes. For this, we must turn to theory.

A large body of theoretical work exists on the subject of H$_2$ formation on grains (see, for example, the review of Pirronello et al. 2000 and the many references therein), stretching back almost 40 years to the pioneering work of Gould & Salpeter (1963). In a highly influential paper, Hollenbach, Werner, & Salpeter (1971) parameterized the H$_2$ formation rate as

$$R = 0.5 \bar{v}_H \sigma_d S f_a n_H n_d , \qquad (30)$$

where n_d is the number density of dust grains, σ_d is their mean geometric cross section, $\bar{v}_H$ is the mean velocity of the hydrogen atoms striking the grains, S is the sticking coefficient (the probability that a hydrogen atom striking the grain will stick to the surface), and f_a is the fraction of adsorbed hydrogen atoms that actually form H$_2$, rather than simply escaping back into the gas phase. They argued that for gas and grain temperatures typical of molecular clouds, both S and f_a should be of the order of unity.

Hollenbach & McKee (1979) later used this prescription to derive an H$_2$ formation rate for the local ISM that continues to be widely cited:

$$k_9 = 3 \times 10^{-17} \frac{T_2^{0.5} f_a}{y} \ \mathrm{cm^3 \ s^{-1}} , \qquad (31)$$

where

$$y = 1 + 0.4\sqrt{T_2 + T_{gr,2}} + 0.2 T_2 + 0.08 T_2^2 \qquad (32)$$

and where T_2 and $T_{gr,2}$ are the gas and grain temperatures in units of 100 K. They argued that f_a should be approximately constant and of the order of unity for grain temperatures below some critical value T_{cr}, but that for $T_{gr} > T_{cr}$, it should fall off exponentially, with most of the hydrogen atoms evaporating from the grain surface before they have time to form H$_2$. The value of T_{cr} has proved difficult to determine precisely but is of the order of 100 K.

Although this rate has been widely adopted in the literature, recent experiments have cast doubt on its validity at high temperatures and suggest that the H$_2$ formation rate may be smaller than previously assumed (Pirronello et al. 1997a, 1997b, 1999; Katz et al. 1999; Biham et al. 2001). However, since this conclusion is not entirely clear (Cazaux & Tielens 2002) and their work is still ongoing, I have

3. COMPARING THE DIFFERENT MODES OF FORMATION

We can combine equations (19) and (23) to write the total gas-phase H_2 formation rate as

$$R_{H_2,gas} = R_{H_2,H^-} + R_{H_2,H_2^+} , \qquad (33)$$

while the grain-catalyzed rate can be written as

$$R_{H_2,dust} = k_9 n_{tot} n_H \left(\frac{D}{D_{MW}} \right) , \qquad (34)$$

where n_{tot} is the total particle number density, D is the dust-to-gas ratio, and D_{MW} is its value in the local ISM.

Combining these equations, we can easily solve for the dust-to-gas ratio at which $R_{H_2,gas}$ and $R_{H_2,dust}$ are equal, which I denote as D_{cr}:

$$D_{cr} = \frac{R_{H_2,gas}}{k_9 n_{tot} n_H} D_{MW} . \qquad (35)$$

In the common case in which $R_{H_2,H^-} \gg R_{H_2,H_2^+}$, this equation reduces to

$$D_{cr} = \frac{k_1}{k_9} \frac{x}{1 + x/x_{cr} + f_{rad}} D_{MW} , \qquad (36)$$

where x_{cr} and f_{rad} are given by equations (11) and (14), respectively. A similar equation can be written in the much less common case in which $R_{H_2,H_2^+} \gg R_{H_2,H^-}$.

In order to help illustrate the behavior of these equations, I plot in Figures 1–4 the value of D_{cr} as a function of temperature for gas illuminated by the Mathis et al. (1983) radiation field in four different scenarios: low-ionization, low-density gas ($x = 10^{-4}$, $n_H = 1$ cm^{-3}; Fig. 1), low-ionization, high-density gas ($x = 10^{-4}$, $n_H = 10^3$ cm^{-3}; Fig. 2), high-ionization, low-density gas ($x = 10^{-2}$, $n_H = 1$ cm^{-3}; Fig. 3), and high-ionization, high-density gas ($x = 10^{-2}$, $n_H = 10^3$ cm^{-3}; Fig. 4). In each case, I adopt a fixed grain temperature $T_{gr} = 20$ K, although small changes in T_{gr} have little effect on the results provided that it remains less than T_{cr}.

A striking feature of these plots is the strong temperature dependence of D_{cr}. At low temperatures, grain-catalyzed H_2 formation is relatively efficient, and very little dust is needed before grain catalysis dominates. Above a few hundred kelvins, however, the efficiency of grain catalysis decreases significantly, while the efficiency of gas-phase H_2 formation continues to grow. As a result, the required dust abundance rises sharply with increasing temperature.

4. ASTROPHYSICAL EXAMPLES

From the behavior outlined in Figures 1–4, it is clear that gas-phase H_2 formation is at its most effective in warm, dense gas with a high fractional ionization. However, most of the molecular gas that we observe in our Galaxy is in the form of molecular clouds with low temperatures ($T \sim 20$ K) and very low fractional ionizations ($x \sim 10^{-7}$), and in these conditions grain-catalyzed formation dominates by many orders of magnitude.
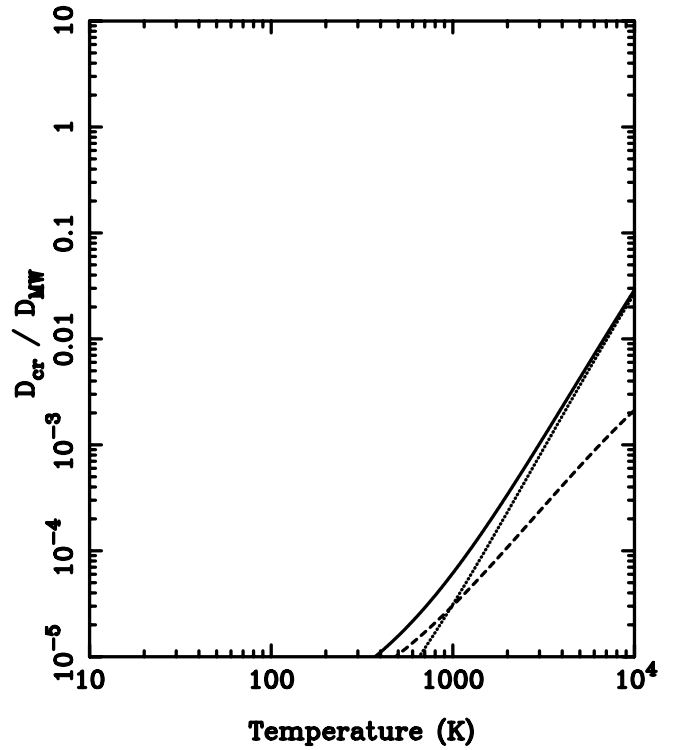

Fig. 1.—D_{cr} as a function of temperature for low-ionization, low-density gas ($x = 10^{-4}$, $n_H = 1$ cm^{-3}). The solid line is the value of D_{cr} given by eq. (35); the dashed and dotted lines are the contributions to this value of H^- and H_2^+, respectively.

A more promising place to look for gas-phase H_2 formation is in the so-called warm neutral medium (WNM). In models of the multiphase ISM that assume thermal pressure equilibrium between phases (Field, Goldsmith, & Habing 1969; McKee & Ostriker 1977; Wolfire et al. 1995), this is predicted to have a temperature of approximately 8000 K, high enough to collisionally dissociate H_2. However, recent observations (Heiles & Troland 2002) and simulations that include the effects of turbulence (Gazol et al. 2001; Mac Low et al. 2001) suggest that much of this gas is actually at much lower temperatures; for instance, Heiles & Troland quote a temperature range of 500 K < T < 5000 K.

Taking representative values for the temperature and ionization of the WNM to be $T = 2000$ K and $x = 10^{-2}$ (Heiles 2001), I find that

$$\frac{D_{cr}}{D_{MW}} = \frac{4.1}{2.7 + f_{rad,H^-}} + \frac{0.047}{1.1 + f_{rad,H_2^+}} . \qquad (37)$$

In other words, gas-phase formation would dominate if we could ignore the effects of the radiation field. In practice, this is not possible; at the densities characteristic of the WNM ($n \simeq 0.1$ cm^{-3}), we have

$$f_{rad,H^-} = 3.9 \times 10^3 , \qquad (38)$$

$$f_{rad,H_2^+} = 1.0 \times 10^2 , \qquad (39)$$

and equation (37) becomes

$$D_{cr} = 5.2 \times 10^{-3} D_{MW} . \qquad (40)$$

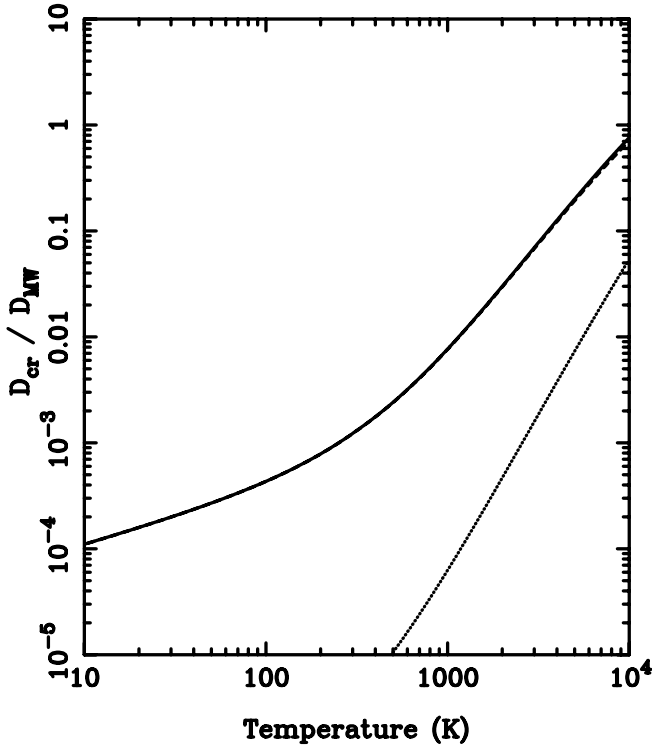FIG. 2.—As in Fig. 1, but for low-ionization, high-density gas ($x = 10^{-4}$, $n_{\mathrm{H}} = 10^3$ cm^{-3}).

FIG. 3.—As in Fig. 1, but for high-ionization, low-density gas ($x = 10^{-2}$, $n_{\mathrm{H}} = 1$ cm^{-3}).

These two examples demonstrate that gas-phase H₂ formation is unimportant in the bulk of the gas in the Milky Way: either the temperature and ionization are too low, as in molecular clouds, or the gas is too diffuse and H₂ formation is suppressed by the photodissociation of H⁻ and H₂⁺.

However, there are a few counterexamples. For instance, gas-phase H₂ formation has long been known to play an important role in the chemistry of nova ejecta (Rawlings 1988) and protostellar outflows (Glassgold, Mamon, & Huggins 1989), where the gas initially has little or no dust (although more generally forms later) and where the high gas densities help mitigate the effects of photodissociation. Gas-phase formation is also predicted to dominate the molecular chemistry of freely expanding supernova remnants such as SN 1987A (Culhane & McCray 1995). Finally, Lepp & McCray (1983) suggest that gas-phase formation may dominate in X-ray dissociation regions (dense clouds illuminated by hard X-rays); modeling by Maloney, Hollenbach, & Tielens (1996) would appear to confirm this.

These are somewhat unusual conditions, however, and in general dust abundances significantly below the typical Galactic value are required before gas-phase H₂ formation becomes competitive with grain-catalyzed formation.

One place in which we might expect to find these low dust abundances is in the metal-poor gas within dwarf galaxies. Kamaya & Hirashita (2001) examine a well-studied example, the metal-poor dwarf I Zw 18, and show that provided that its neutral ISM is clumpy (with clump densities $n \gtrsim 100$ cm^{-3}) and moderately ionized ($x \sim 10^{-3}$), then gas-phase formation will dominate. They also show that the formation of H₂ in this manner would not conflict with the upper limit on the H₂ column density of I Zw 18 obtained by *FUSE* (Vidal-Madjar et al. 2000), because of the small filling factor of the clumps.
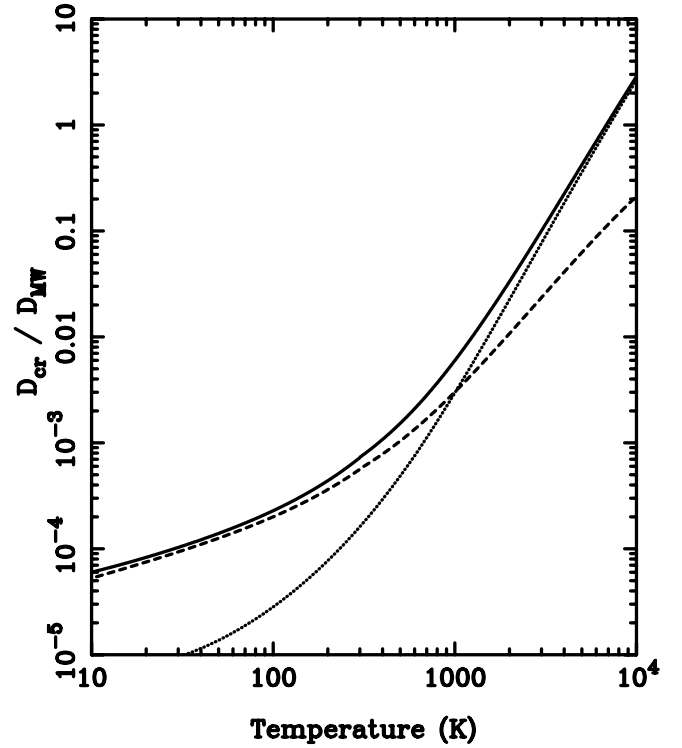
Another place we might look for significant gas-phase H₂ formation is in damped Lyα (DLA) systems, many of which have low dust abundances (see, e.g., Lopez et al. 2002). An interesting example is the absorber at $z = 3.025$ in the spectrum of Q0347−3819 recently studied by Levshakov et al. (2002). This system has a temperature $T \simeq 400$ K (as inferred from the Doppler broadening of its many associated H₂ and metal absorption lines) and a fractional ionization $x \simeq 2 \times 10^{-5}$. If we assume that H⁻ photodetachment is negligible, we find that for this system,

$$D_{\mathrm{cr}} = 4.6 \times 10^{-4} D_{\mathrm{MW}} \; . \qquad (41)$$

Comparing this with a measured dust-to-gas ratio of $D \simeq 0.05 D_{\mathrm{MW}}$, we see that gas-phase H₂ formation contributes no more than about 1% of the total H₂ in this system. Including the effects of radiation merely strengthens this conclusion.

There is no reason to suspect that this situation is particularly unusual; all DLAs *by definition* have large H I column densities and consequently have small fractional ionizations. We would therefore expect grain catalysis to dominate in these systems.

Finally, gas-phase H₂ formation has long been known to play an important role in the early stages of galaxy formation. In primordial gas, this is obvious: there is no dust, so any H₂ that forms *must* form in the gas phase. A more interesting problem is determining the value of D_{cr} for these systems; in other words, at what point does grain-catalyzed formation overtake gas-phase formation?

For the purposes of this discussion, I adopt the example of an H₂-cooled protogalaxy with temperature $T = 1000$ K and fractional ionization $x = 2 \times 10^{-4}$ (Tegmark et al. 1997). These values are appropriate for the first generation
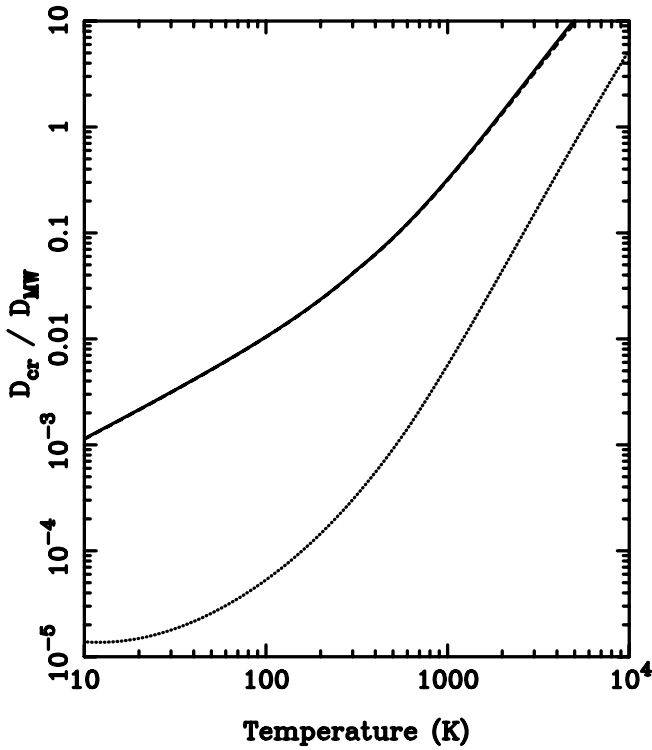
FIG. 4.—As in Fig. 1, but for high-ionization, high-density gas ($x = 10^{-2}$, $n_H = 10^3$ cm^{-3}).

of star-forming protogalaxies, and while they may be underestimates for later generations, my analysis can easily be rescaled for higher values. For this example protogalaxy, I find that

$$\frac{D_{cr}}{D_{MW}} = \frac{2.1 \times 10^{-2}}{1 + f_{rad,H^-}} + \frac{1.3 \times 10^{-4}}{1 + f_{rad,H_2^+}} . \tag{42}$$

Thus, if the radiation field is unimportant, $D_{cr} \simeq 0.02 D_{MW}$, comparable to the values seen in some metal-poor dwarf galaxies at the present day (Lisenfeld & Ferrara 1998).

How strong is the radiation field within a protogalaxy? There are potentially three main contributors to this field: the protogalaxy's own stellar population, emission from neighboring galaxies, and radiation from the cosmological background produced by distant sources. It is simplest to consider these separately.

Much of the optical and near-infrared radiation responsible for destroying H$^-$ and H$_2^+$ is produced by long-lived stars, and so the contribution of the protogalaxy's stellar population depends as much on its star formation history as on its current star formation rate. This makes it very difficult to parameterize its effects in the general case; it is much easier to examine a simple example that is hopefully broadly representative.

For the purposes of this example, I assume the following:

1. The protogalaxy underwent an instantaneous (or near-instantaneous) starburst 10^8 yr ago, following which it formed no more stars.

2. The stars that did form are located in the center of the protogalaxy, within a small enough region that I can approximate their emission as coming from a point source.

3. The luminosity and spectral energy distribution of this stellar cluster are well described by the $Z = 0.05 \, Z_\odot$ model of Leitherer et al. (1999).

4. The protogalaxy itself is well described by a truncated isothermal sphere density profile (Iliev & Shapiro 2001).

All of these assumptions are debatable, but they do provide us a basis on which to estimate the effects of the stellar radiation field. Moreover, these assumptions are somewhat conservative and tend to minimize the effectiveness of the stellar radiation. For instance, if we reduce the time since the starburst from 10^8 to 10^7 yr, then the photodetachment rate increases by a factor of 50. Similarly, if we assume continuous star formation rather than an instantaneous starburst, then we obtain a similar (or slightly larger) photodetachment rate once the total mass of stars formed has reached a comparable level.

We could also criticize the adoption of the Leitherer et al. (1999) model on the basis that it assumes a standard Salpeter initial mass function (IMF), while there is considerable evidence that the primordial IMF is biased toward high masses (Larson 1998). However, this again means that we would underestimate the photodetachment rate (although we would significantly overestimate the lifetime of the stellar population).

Returning to my example, the first two assumptions allow me to write the H$^-$ photodetachment rate at a distance R from the stars as

$$k_6 = \frac{1}{R^2} \int_{\nu_{th}}^{\nu_0} \frac{\sigma_\nu L_\nu}{h\nu} \, d\nu , \tag{43}$$

where L_ν, the stellar luminosity per unit frequency, is given by the Leitherer et al. model. Using this value, I obtain

$$k_6 = 4.9 \times 10^{-8} F(M_*, R) \, s^{-1} , \tag{44}$$

where

$$F(M_*, R) = \left(\frac{M_*}{10^6 \, M_\odot}\right) \left(\frac{R}{1 \text{ kpc}}\right)^{-2} \tag{45}$$

and where M_* is the mass of stars formed in the starburst. Similarly, we can write the H$_2^+$ photodissociation rate as

$$k_8 = 9.4 \times 10^{-10} F(M_*, R) \, s^{-1} , \tag{46}$$

and from these rates calculate f_{rad,H^-} and f_{rad,H_2^+}:

$$f_{rad,H^-} = 40 n_H^{-1} F(M_*, R) , \tag{47}$$

$$f_{rad,H_2^+} = 1.5 n_H^{-1} F(M_*, R) . \tag{48}$$

By comparing these values and equation (42), we can see that formation via H$_2^+$ contributes at most about 10% of the H$_2$ produced in the gas phase, with the rest coming from H$^-$.

To evaluate these numbers, I use the fact that for a truncated isothermal sphere,

$$n_H \left(\frac{R}{1 \text{ kpc}}\right)^2 \simeq 6.9 \times 10^{-3} \frac{\Omega_b}{\Omega_m} \tag{49}$$

in regions outside of the core. The final unknown M_* can be written as

$$M_* = 1.5 \times 10^7 \epsilon_* (1 + z)^{-3/2} \left(\frac{\Omega_b}{\Omega_m^{3/2} h}\right) M_\odot , \tag{50}$$

where ϵ_* is the star formation efficiency of the protogalaxy, z is its redshift of formation, and h is the Hubble constant in units of 100 km s^{-1} Mpc^{-1}.

For a protogalaxy that formed in a standard Λ-dominated cold dark matter cosmology ($\Omega_m = 0.3$, $\Omega_b = 0.04$, $h = 0.7$) at a redshift $z = 10$ and that formed stars with an efficiency $\epsilon_* = 0.01$, we find that

$$D_{cr} \simeq 3.8 \times 10^{-4} D_{MW} . \tag{51}$$

Thus, in this particular example, radiation from the existing stellar population reduces D_{cr} by almost 2 orders of magnitude.

In view of the uncertainties involved in producing this estimate, it would be unwise to overgeneralize. However, since my assumptions verge on the conservative side, it seems likely that in realistic protogalactic models we would see similar effects and that gas-phase H$_2$ formation would rapidly be overtaken by grain-catalyzed formation.

What about protogalaxies that have yet to form stars? In this case, there is no significant local contribution to the radiation field, which instead is produced by neighboring sources and/or the cosmological background.

For neighboring sources, we can reuse the above formalism, as long as we set R to the distance to the extragalactic source. However, this is typically an order of magnitude or more greater than the size of a protogalaxy, implying that the effect of the radiation will be *at least* 2 orders of magnitude smaller than the effects discussed above. Consequently, radiation from protogalaxies of the size discussed here will have little or no effect on gas-phase H$_2$ formation within their neighbors, unless their emitted flux is substantially larger than has been assumed here.

For the background, we again face the problem that any conclusions that we can draw are strictly limited by our poor knowledge of the star formation history, this time on a cosmological rather than protogalactic scale. The best that we can do is to determine how strong the background needs to be before it has a significant effect. Modeling the background below the Lyman limit as a power law,

$$J_\nu = J_{21} \left(\frac{\nu_0}{\nu} \right)^\alpha , \tag{52}$$

where $J_{21} = 10^{-21}$ ergs s^{-1} cm^{-2} Hz^{-1} sr^{-1} and where $h\nu_0 = 13.6$ eV, I find that for $\alpha = 1$,

$$k_6 = 8.1 \times 10^{-10} J_{21} \text{ s}^{-1} , \tag{53}$$

and hence

$$f_{rad,H^-} = 0.6 J_{21} n_H^{-1} . \tag{54}$$

The significance of the background varies with n_H and hence with position within the protogalaxy. For my example protogalaxy, formed at a redshift $z = 10$, gas near the truncation radius has a density $n_H \sim 7 \times 10^{-3}$ cm^{-3} and thus is affected for $J_{21} \gtrsim 0.01$; on the other hand, gas in the central core has $n_H \sim 1$ cm^{-3} and is only affected for $J_{21} \gtrsim 1$.

5. CONCLUSIONS

The simplicity of the basic chemistry involved in gas-phase H$_2$ formation means that it is easy to construct a fairly accurate expression for the formation rate in terms of only a few parameters: the temperature, density, and fractional ionization of the gas, plus the strength of the radiation field near the H$^-$ and H$_2^+$ photodissociation thresholds. Expressions for the rate of H$_2$ formation via the H$^-$ and H$_2^+$ ions are given by equations (19) and (23), respectively, and the total formation rate is simply the sum of these two values.

Using these expressions, together with an analytical expression for the grain-catalyzed H$_2$ formation rate, one can solve for D_{cr}, the dust-to-gas ratio required for grain-catalyzed H$_2$ formation to overtake gas-phase formation. The results demonstrate that, in principle, gas-phase H$_2$ formation could be comparable to grain-catalyzed formation in galactic gas, particularly at high temperatures at which the latter is inefficient. In practice, however, it is usually significantly slower, either because of a shortage of free electrons and protons (which reduces the formation rate of the intermediate ions) or because the incident radiation field destroys the ions before they have a chance to form H$_2$.

Finally, in order to demonstrate the simplicity and potential utility of this approach, I have applied it to a number of astrophysical examples. Not surprisingly, I find that in most cases D_{cr} is significantly less than the mean Galactic value, often by several orders of magnitude. Nevertheless, there are counterexamples, such as X-ray photodissociation regions (Lepp & McCray 1983; Maloney et al. 1996), nova ejecta (Rawlings 1988), or the high-redshift protogalaxies analyzed in detail here. A common thread linking many of these exceptions seems to be the fact that they have dust-to-gas ratios (but not necessarily metallicities) significantly lower than the mean Galactic value.

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