The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/35447

Please be advised that this information was generated on 2017-07-24 and may be subject to change.
1. INTRODUCTION

The formation of H$_2$ from a pair of neutral hydrogen atoms in the presence of a radiation field can be brought about by a Raman association process. Its efficiency depends on the spectrum and the intensity of the radiation field, and it varies as the square of the hydrogen atom density. The process is likely to contribute to H$_2$ formation in dense atomic gas subjected to strong Lyman or Werner band systems. In photon-dominated regions the ultraviolet photons may dissociate the molecules, but with increasing depth into the gas, the corresponding optical depths become large and the H$_2$ molecules are self-shielding. The optical depth for Raman association process. Its efficiency depends on the spec-


ABSTRACT

We investigate the contribution that Raman association makes to H$_2$ production in the early universe at redshifts $10 \leq z \leq 10^4$. The Raman process involves inelastic scattering of electromagnetic radiation off two colliding hydrogen atoms, taking away kinetic and binding energy and leaving bound H$_2$. We calculate the inelastic cross sections and rate coefficients for this process and determine the Raman association rate in the cosmic background radiation field present during the early stages of the universe. A comparison with other H$_2$-forming reactions is made.

Subject headings: astrochemistry — early universe — ISM: molecules — molecular processes — radiation mechanisms: general — scattering

2. THEORY AND METHOD

Raman association is an inelastic scattering process, in which electromagnetic radiation of energy $h\omega$ scatters off two colliding H(3S) atoms and causes a transition from the continuum to a bound state of H$_2$(3$\Sigma^+_g$). Kinetic and binding energy $h(\omega_e - \omega)$ is transferred to the radiation field in the process

$$H(3S) + H(3S) + h\omega \rightarrow H_2(3\Sigma^+_g) + h\omega_e.$$  

(1)

The H$_2$ production rate for this process is given by an Arrhenius-type equation:

$$\frac{dn(H_2)}{dt} = k(T_m, T_c)n(H)^2.$$  

(2)
TABLE 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{H}^+ + \text{H} \rightarrow \text{H}_2 + e^- )</td>
</tr>
<tr>
<td>2</td>
<td>( \text{H}^+ + \text{H} \rightarrow \text{H}_2^+ + \hbar \omega )</td>
</tr>
<tr>
<td>2b</td>
<td>( \text{H}_2^+ + \text{H} \rightarrow \text{H}_2^+ + \text{H}^+ )</td>
</tr>
<tr>
<td>2c</td>
<td>( \text{H}_2^+ + e^- \rightarrow \text{H} + \text{H} )</td>
</tr>
<tr>
<td>2d</td>
<td>( \text{H}_2^+ + h\omega \rightarrow \text{H}^+ + \text{H} )</td>
</tr>
<tr>
<td>3</td>
<td>( \text{H}_2^+ \rightarrow \text{H}_2 )</td>
</tr>
<tr>
<td>3e</td>
<td>( \text{H}_2 \rightarrow \text{H} + \text{H} )</td>
</tr>
<tr>
<td>3f</td>
<td>( \text{H}^+ \rightarrow \text{H}_2 + \hbar \omega )</td>
</tr>
<tr>
<td>3g</td>
<td>( \text{H} + \text{H} + \hbar \omega \rightarrow \text{H}_2 + \hbar \omega )</td>
</tr>
</tbody>
</table>

**Note.** All rate constants are taken from Stancil et al. (1998) except No. 2d, taken from Sauval & Tatum (1984), and No. 4, from this work.

To examine convergence of the integral \( \int \omega \psi_j(\omega)\sigma(E, \omega) \) in equation (3), we increased the number of points in the spectrum. We did this by taking the logarithm (base 10) of the cross sections and using cubic spline interpolation from resonance to resonance, after which the interpolated values are exponentiated. A stable interpolation without oscillations was obtained.

FIG. 1.—Total Raman association cross section in atomic units of area per energy, as a function of photon energy. The collision energy is 0.448 eV, and the initial rotational quantum number \( J = 6 \). The bars indicate the occurrence of rovibrational resonances associated with the indicated excited electronic state.

**3. EARLY UNIVERSE**

We investigate the importance of Raman association of \( \text{H}_2 \) in the early universe by comparing the rate of association with a number of other important \( \text{H}_2 \)-forming processes. We considered (see Table 1) associative detachment of \( \text{H}^+ \) and \( \text{H} \), radiative association of \( \text{H}^+ \) and \( \text{H} \) followed by reaction with \( \text{H} \), competing with dissociative recombination, photodissociation of \( \text{H}_2^+ \), and reaction of \( \text{H}_2^+ \) with \( \text{H}^+ \), radiative association of excited and ground-state hydrogen, and Raman association. The production rates follow from simple reaction kinetics. We use densities of \( \text{H}, \text{H}^+, \text{H}^+, \text{H}^+ \), and gas and radiation temperature as a function of redshift, as computed by Stancil et al. (1998). During the early stages of the universe, after recombination but before formation of the first stars, the radiation temperature decreases from about 10^4 K at \( z \approx 10^6 \) to 10 K at \( z \approx 10 \), and the gas temperature decreases from about 10^3 to 10^{-3} K. The total gas density decreases from approximately 10^3 to 10^{-3} cm^-3.

**4. RESULTS**

In Figure 1, we show the total Raman association cross section \( \sum_j \sigma_j(\omega) \) for two \( \text{H}(S) \) atoms, colliding at a kinetic energy of \( E = 0.448 \) eV, with rotational quantum number \( J = 6 \) (the most populated rotational state at gas temperatures of \( \approx 4000 \) K), as a function of photon energy. At lower photon energies, the cross section varies smoothly with \( \omega \), but as the photon energy increases, the resonances come to dominate the spectrum. At a resonance the cross section is typically increased by 5 to 10 orders of magnitude with respect to the background. Because of the closeness of resonances, the background cross section in the resonant region is increased by about 4 orders of magnitude as compared with the off-resonant region. The
horizontal bars in Figure 1 indicate where the rovibrational resonances of different electronic intermediate states are found. At about $8 \times 10^4$ cm$^{-1}$, the cross section decreases dramatically. The reason is that at these photon energies, the dissociation limit of the $B^1\Sigma_u^+$, $B^1\Sigma_u^-$, and $C\Pi_u$ states is reached, and there are no bound states close in energy. As the photon energy increases further, the bound states of the $B''^1\Sigma_u^+$, $D''^3\Pi_u$, and $D'\Pi_u$ states are reached, and the cross section is enhanced again. The second sharp decrease in the spectrum occurs at $\sim 9.4 \times 10^4$ cm$^{-1}$, the dissociation limit of these states. Figure 2 shows the Raman association rate constant as a function of matter temperature ($T_m$) and radiation temperature ($T_r$). The rate constant decreases with increasing matter temperature because although the collision rate increases with temperature, the shorter H-H interaction time per collision reduces the cross section for Raman association significantly. The rate constant drops about 4 orders of magnitude as the gas temperature increases from 10 to $10^4$ K. The dependence on radiation temperature is much stronger, and the rate constant increases steeply as the radiation temperature becomes higher. From 10 to $\sim 2700$ K, the rate constant increases by as much as 20 orders of magnitude. At $T_r \approx 2700$ K, the increase with temperature becomes stronger: from 2700 to $10^5$ K, the rate constant increases by about 10 orders of magnitude. The reason is that at high radiation temperatures, high-energy photons become available, so that the cross sections, and thus the rate constants, are significantly enhanced by the resonances.

In Figure 3, the $H_2$ production rates for the processes in Table 1 are shown as a function of redshift. The Raman association rate (dashed line) has a maximum at $z \approx 1385$, when both the radiation and matter temperature are about 3800 K. At this time, the Raman association rate is comparable to the other $H_2$-producing processes. The maximum is due to the competition between the increasing availability of atomic hydrogen, caused by the recombination of protons with electrons, and the decreasing radiation temperature. At $z \approx 10^3$, the Raman association rate starts decreasing more slowly with time. Although both radiation and matter temperature drop below 2750 K here, it is the decrease in $T_r$ that causes the change in behavior. At later times the $H_2$ production is completely taken over by the $H^+$-catalyzed process and the associative detachment of $H^+$ and H.

We conclude that at $400 \leq z \leq 2600$, a significant amount of the existing $H_2$ was produced by Raman association. At $z \approx 1600$, as much as 25% of $H_2$ present at that time was produced by Raman association, the remaining 75% coming mainly from radiative association of excited H with H.

The integrated contribution of Raman association to the $H_2$ production at $z \approx 10$ is about 0.01%, which is not much smaller than the contribution made by radiative association of excited and ground-state hydrogen ($\sim 0.08\%)$.

5. CONCLUSIONS

We investigate the rate of association of molecular hydrogen by means of a Raman scattering process. We present the first calculation of the corresponding inelastic scattering cross section over a wide range of photon and collision energies, in which all relevant rovibrational resonances are included. From these cross sections we obtain the Raman association rate constant as a function of matter and gas temperature, and we use these rate constants to evaluate the rate of Raman association under conditions present in the early universe. We show that the contribution to $H_2$ production around $z \approx 1600$ is significant. The total contribution to the $H_2$ production up to $z = 10$ is comparable to the contribution made by radiative association of excited and ground-state H atoms: on the order of 0.01%. We show that it is crucial to take into account the effect of resonances at high radiation temperatures in various astrophysical circumstances.

The work of A. D. is supported by a grant from the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences, Office of Science, US Department of Energy. M. v. d. L. thanks the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) for financial support. We are greatly indebted to Stephen Lepp for providing the details of the cosmological model. M. v. d. L. thanks Gerrit Groenenboom for useful discussions.
REFERENCES


van der Loo, M. P. J., Groenenboom, G. C., Jamieson, M. J., & Dalgarno, A.