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RECOMBINATION OF H₂ BY RAMAN ASSOCIATION IN THE EARLY UNIVERSE

Alex Dalgarno

Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138; dalgarno@cfa.harvard.edu

and

Mark P. J. van der Loo

Institute of Theoretical Chemistry, Radboud Universiteit Nijmegen, Toernooiveld 1,
NL-6525 ED Nijmegen, Netherlands; m.vanderloo@theochem.ru.nl

ABSTRACT

We investigate the contribution that Raman association makes to H₂ production in the early universe at redshifts $10 \le z \le 10^4$. The Raman process involves inelastic scattering of electromagnetic radiation off two colliding hydrogen atoms, taking away kinetic and binding energy and leaving bound H₂. 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 H₂-forming reactions is made.

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

1. INTRODUCTION

The formation of H₂ 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 H₂ formation in dense atomic gas subjected to intense radiation fields at wavelengths longer than the threshold wavelengths for absorption in the Lyman and 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 H₂ molecules are self-shielding. The optical depth for Raman association is small. Raman association may also contribute to the formation of H₂ in the high atmospheres of hot Jupiters and generally in regions of atomic hydrogen subjected to strong Lyα radiation.

The formation of H₂ was a source of structure in the early universe. As an example of the process of Raman association, we calculate its contribution to the formation of H₂ and compare it with those of other processes that have been taken into account in models of the evolution of the universe (Galli & Palla 1998; Lepp et al. 2002).

2. THEORY AND METHOD

Raman association is an inelastic scattering process, in which electromagnetic radiation of energy $\hbar\omega$ scatters off two colliding $H(^2S)$ atoms and causes a transition from the continuum to a bound state of $H_2(^1\Sigma_g^+)$. Kinetic and binding energy $\hbar(\omega_{sc} - \omega)$ is transferred to the radiation field in the process

$$H(^2S) + H(^2S) + \hbar\omega \rightarrow H_2(^1\Sigma_g^+) + \hbar\omega_{sc}. \quad (1)$$
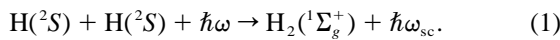
The H₂ production rate for this process is given by an Arrhenius-type equation:

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

where the rate constant k depends on the matter temperature T_m and radiation temperature T_r, and the $n(X)$ are number densities per cubic centimeter. The rate constant is related to the Raman scattering cross section σ via the following relation:

$$k(T_m, T_g) = \frac{gcV}{2} \sum_f \int dE\, d\omega\, P_{T_m}(E)\rho_{T_r}(\omega)\sigma_{fi}(E,\omega), \quad (3)$$

where $g = \frac{1}{4}$ takes into account that three-quarters of all collisions take place on the $H_2(^3\Sigma_g^+)$ surface and do not add to the Raman association rate. In equation (3), c is the speed of light, V is unit volume, and the factor of $\frac{1}{2}$ is introduced because the rate of association (eq. [2]) is expressed in H-atom density, rather than H-H pair density. The matter temperature dependence is determined by the Boltzmann distribution $P_{T_m} = (2J + 1) \exp{(-E/k_B T_m)}V^{-1}\lambda_0^3$ with J the rotational quantum number and $\lambda_0 = (2\pi\hbar^2/\mu k_B T_m)^{1/2}$ the thermal de Broglie wavelength, while μ is the reduced mass of the hydrogen molecule. The dependence on radiation temperature is determined by the Planck photon number density distribution: $\rho_{T_r}(\omega) = \omega^2[2\pi c^3(\exp{\hbar\omega} - 1)]^{-1}$. The cross section depends on the collision energy E and the photon energy ω and is given by

$$\sigma_{fi}(E, \omega) = \frac{8\pi\alpha^2\omega\omega_{sc}^3}{9c^2e^4} S_{fi}(E, \omega), \quad (4)$$

where α is the fine-structure constant, e the elementary charge, and S the Raman scattering matrix, given by the Kramers-Heisenberg equation:

$$S_{fi}(E, \omega) = \sum_{pq} \left| \sum_m \frac{\langle f|\hat{\mu}_p|m\rangle\langle m|\hat{\mu}_q|i\rangle}{\omega_{mi} - \omega + i\Gamma_m} + \frac{\langle f|\hat{\mu}_q|m\rangle\langle m|\hat{\mu}_p|i\rangle}{\omega_{fm} + \omega} \right|^2,$$

where $\omega_{xy} = \omega_x - \omega_y$, the coherent sum runs over the complete set of intermediate states $|m\rangle$, Γ_m is the inverse lifetime of state $|m\rangle$, and the $\hat{\mu}_x$ are components of the dipole operator. Since the initial state $|i\rangle$ lies in the continuum of the electronic ground state of H₂, the cross section is in units of area divided by energy. The ket $|f\rangle$ designates a rovibrational bound state in

TABLE 1
PROCESSES CONTRIBUTING TO THE FORMATION
OF H_2 IN THE EARLY UNIVERSE

No.	Process
1	$H^- + H \rightarrow H_2 + e^-$
2a	$H^+ + H \rightarrow H_2^+ + \hbar\omega$
2b	$H_2^+ + H \rightarrow H_2 + H^+$
2c	$H_2^+ + e^- \rightarrow H + H$
2d	$H_2^+ + \hbar\omega \rightarrow H^+ + H$
2e	$H_2^+ + H^- \rightarrow 3H$
3	$H^* + H \rightarrow H_2 + \hbar\omega$
4	$H + H + \hbar\omega \rightarrow H_2 + \hbar\omega'$

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.

the $X\,^1\Sigma_g^+$ ground state of H_2. In the case of low photon energy, $\omega \ll \omega_{mi}$, the Kramers-Heisenberg formula is approximated by the Placzek-Teller model:

$$S_{fi}^{PT}(E, \omega) = \tfrac{1}{9}\,|\langle f|\,\alpha_\parallel + 2\alpha_\perp\,|i\rangle|^2 + B_{fi}|\langle f|\,\alpha_\parallel - \alpha_\perp\,|i\rangle|^2, \quad (5)$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the parallel and perpendicular components of the polarizability tensor of H_2 in the electronic ground state and B_{fi} is a factor depending on the initial and final rotational angular momentum quantum numbers (van der Loo et al. 2006).

The first term in equation (5) gives rise to resonances when $\omega = \omega_{mi}$, which are not described by the Placzeck-Teller formula. Evaluation of equation (5) is difficult because of the slow convergence of the sum over intermediate states in off-resonance regions. Since the contribution of high-lying electronic states can be considered independent of photon energy, we truncate the sum over m in equation (5), and we use information obtained by evaluating the Placzek-Teller equation in regions that are far off resonance to correct for these missing states.

The computational method we use to calculate the cross sections is described in detail in van der Loo et al. (2006). Briefly, we work in the Born-Oppenheimer approximation, expressing the wave functions as a product of nuclear and electronic states. We neglect the second term in equation (5) and truncate the sum over electronic intermediate states after six states, three of $^1\Sigma_u^+$ and three of $^1\Pi_u$ symmetry. The sum (and integral) over intermediate bound (and continuum) states is then evaluated by expressing the first term of equation (5) as an integral over a Green's function, which is represented using a sinc function discrete variable (sinc-DVR) representation (Colbert & Miller 1992; Groenenboom & Colbert 1993). The contribution of continuum intermediate nuclear states is taken into account using an absorbing boundary condition on the Green's function (Seideman & Miller 1992). In this way, all rovibrational resonances in the lowest six optically allowed electronic intermediate states have been taken into account. In total, we find about 350 rovibrational resonances, depending on the initial state's rotational quantum number. The cross section is computed at a large number ($>1.2 \times 10^4$) of photon energies, in order to obtain a satisfactory representation of the spectrum.

To examine convergence of the integral $\int d\omega\,\rho_{T_r}(\omega)\sigma(E, \omega)$ 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.
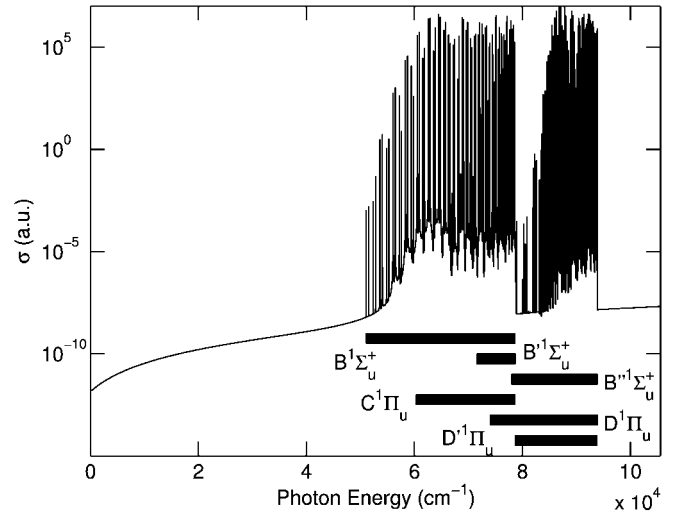

FIG. 1.—Total Raman association cross section in atomic units of area per energy, as a function of photon energy. The collision energy is 0.448 eV, and the initial rotational quantum number $J = 6$. The bars indicate the occurrence of rovibrational resonances associated with the indicated excited electronic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

After integration over the photon energy ω, a smooth function of the collision energy E is obtained. We constructed a satisfactory representation by evaluating it at 20 logarithmically spaced collision energies E, in the range 10^{-6} to 10^{-2} a.u. We use cubic spline interpolation to converge the integral over E in equation (3).

3. EARLY UNIVERSE

We investigate the importance of Raman association of H_2 in the early universe by comparing the rate of association with a number of other important H_2-forming processes. We considered (see Table 1) associative detachment of H^- and H, radiative association of H^+ and H followed by reaction with H, competing with dissociative recombination, photodissociation of H_2^+, and reaction of H_2^+ with H^-, radiative association of excited and ground-state hydrogen, and Raman association. The production rates follow from simple reaction kinetics. We use densities of H, H^-, H^*, 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 $z \approx 10^4$ 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 $\sum_f \sigma_{fi}(E, \omega)$ for two $H(^1S)$ 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 ~4000 K), as a function of photon energy. At lower photon energies, the cross section varies smoothly with ω, 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
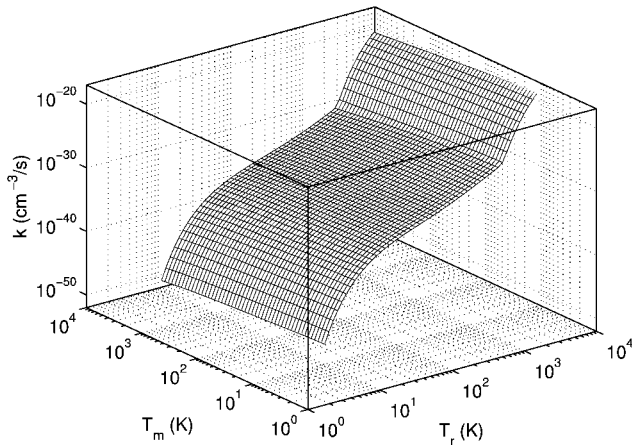
Fig. 2.—Raman association rate constant as function of matter temperature T_m and radiation temperature T_r.

Fig. 3.—H$_2$ production rates as a function of redshift z in the early universe. For the meaning of (1)–(4), see Table 1. The dashed line indicates the Raman association rate in cm^{-3} s^{-1}.

horizontal bars in Figure 1 indicate where the rovibrational resonances of different electronic intermediate states are found. At about 8×10^4 cm^{-1}, the cross section decreases dramatically. The reason is that at these photon energies, the dissociation limit of the $B\ ^1\Sigma_u^+$, $B'\ \Sigma_u^+$, 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 $B''\ ^1\Sigma_u^+$, $D\ ^1\Pi_u$, and $D'\ ^1\Pi_u$ 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 ~ 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 10^4 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 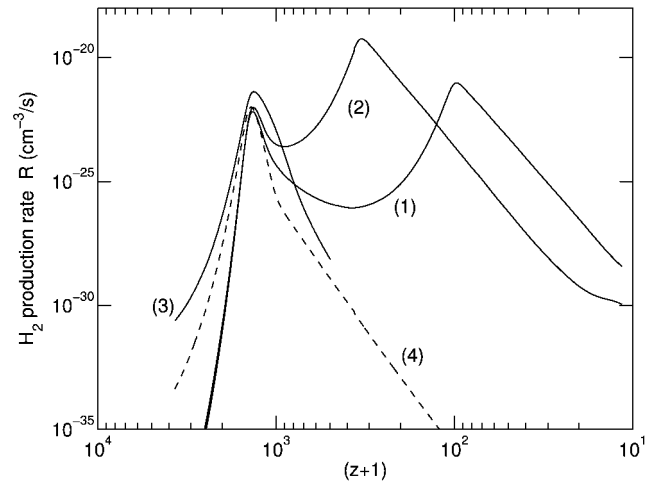later times the H$_2$ production is completely taken over by the H$^+$-catalyzed process and the associative detachment of H$^-$ and H.

We conclude that at $400 \lesssim z \lesssim 2600$, 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 $z = 10$ 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.

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