Abstract

Astrophysical models of primordial star formation require rate constants for three-body recombination as input. The current status of these rates for H$_2$ due to collisions with H is far from satisfactory, with published rate constants showing orders of magnitude disagreement at the temperatures relevant for H$_2$ formation in primordial gas. This letter presents an independent calculation of this recombination rate constant as a function of temperature. An analytic expression is provided for the rate constant which should be more reliable than ones currently being used in astrophysical models.
A recent study by Turk et al. [1] on the effects of varying the three-body recombination (TBR) rate of hydrogen during primordial star formation concluded that “the uncertainty in the three-body H$_2$ formation rate significantly limits our ability to model the density, temperature, and velocity structure of the gas close to the center of the collapse” and “the uncertainty in the outcome of collapse caused by our poor knowledge of the three-body H$_2$ formation rate coefficient cannot be so easily dealt with and represents a major limitation on our ability to accurately simulate the formation of the first stars in the universe.”

In this study, three different published rate constants were used for TBR of H$_2$ due to collision with H. Two of these rate constants were based on shock tube measurements of Jacobs et al. [2] who gave analytic expressions for TBR and the inverse process of collision induced dissociation (CID). The TBR rate adopted by Palla et al. [4] was identical to the expression given by [2]. Flower and Harris [3] used the CID expression given by [2] together with their own determination of the equilibrium constant to derive a very different TBR rate constant. The discrepancy between these two TBR rate constants, therefore, is due to the adopted equilibrium constants that were used. The equilibrium constant used by Flower and Harris [3] relies on the Saha equation and their determination of the H$_2$ partition function. When fitted to a simple temperature dependent function, Flower and Harris found that their value is approximately 4.5 times greater than a similar fit obtained from the JANAF Thermochemical Tables at a temperature of 1000 K. Using this equilibrium constant together with the CID expression given in [2] yielded a TBR rate constant which was approximately 6 times larger at T=1000 K than the TBR expression given in [2].

It appears that there are two separate reasons for the factors of 4.5 and 6 discrepancies at 1000 K. The first reason is fitting error. The experiments were performed in a temperature range of 2900-4700 K. When the same comparisons for the equilibrium constant and TBR rate are made in this experimental temperature range, both discrepancies are reduced to a factor of 4 over the whole range. In order to see this, the exact H$_2$ partition function must be used to compute the equilibrium constant, not the fitted value [3] which is valid only for $T < 2000$ K. The second reason is the choice of atomic partition function which was
assumed to be 2 for hydrogen in its 1s $^2S$ ground state [3]. This choice accounts for the nuclear spin degeneracy but not the electron spin degeneracy. Because the formation of $H_2$ occurs in the singlet electronic ground state, the electron spin degeneracy was assumed to be unity [5]. The present author disagrees with this assumption because 3/4 of the atomic collisions would still occur on the repulsive triplet electronic state even though they do not react. In order to account for only the 1/4 of collisions which can react, the atomic partition function used by Flower and Harris [3] would need to be increased by a factor of 2 which would reduce their equilibrium constant by a factor of 4. Therefore, the TBR rate of Flower and Harris [3] would also need to be reduced by this same factor of 4. This would, upon use of the exact $H_2$ partition function, bring it into excellent agreement with the TBR rate of Jacobs et al. [2] and Palla et al. [4] at temperatures in the experimental range.

While this resolves the discrepancy between two of the three rate constants used in the Turk et al. [1] study, it does not imply that the rate constants are reliable. The experimental paper [2] upon which these TBR rate constants are based, cautions that their data lies in the middle of a range of other experimental data whose values vary over an order magnitude. Furthermore, there is no justification for extrapolating collisional data obtained over a small range of temperatures, to temperatures that lie outside that range. All three of the TBR rates considered in the Turk et al. [1] study are based on extrapolations for temperatures between 300 and 2900 K. The third and smallest TBR rate, those of Abel et al. [6], uses an extrapolation of classical trajectory calculations performed by Orel [7] at temperatures below 300 K. This extrapolation assumes an inverse temperature dependence which resembles that of Palla et al. [4] and consequently has a sudden change in slope at 300 K. It is desirable, therefore, to perform an independent calculation which does not rely on extrapolations and is reliable over the temperature range required by the astrophysical models.

In this letter, we report results of quantum mechanical calculations of TBR rate constants for the collision of three hydrogen atoms in the temperature range $300 < T < 10,000$ K. We use a Sturmian representation which provides a quadrature of the two-body continuum and may be used to generate a complete set of states within any desired TBR pathway [8].
The effective TBR and CID rate constants at local thermodynamic equilibrium (LTE) may then be defined by

\[ k_r \equiv \sum_{b,u} k_{u \rightarrow b} \frac{g_u \exp(-E_u/k_B T)}{Q_H^2 Q_T} \] (1)

\[ k_d \equiv \sum_{b,u} k_{b \rightarrow u} \frac{g_b \exp(-E_b/k_B T)}{Q_H^2} \] (2)

where \( b \) designates a bound state with energy \( E_b \) and \( u \) designates an unbound state with energy \( E_u \). These states are defined by their associated vibrational and rotational quantum numbers \( v \) and \( j \). The statistical factors are given by \( g = (2j + 1)(2I + 1) \) with the nuclear spin \( I = 0 \) for para-H\(_2\) and \( I = 1 \) for ortho-H\(_2\). With this definition for \( g \), the atomic partition function is \( Q_H = 4 \) as described above. The molecular partition function \( Q_{H_2} \) and the translational partition function \( Q_T \) are defined by

\[ Q_{H_2} = \sum_b g_b \exp(-E_b/k_B T) \] (3)

\[ Q_T = \frac{(\pi m k_B T)^{3/2}}{h^3} \] (4)

where \( h \) is Planck’s constant, \( k_B \) is Boltzman’s constant, \( T \) is the temperature, and \( m \) is the mass of H. Detailed balance of the rate coefficients \( k_{b \rightarrow u} \) and \( k_{u \rightarrow b} \) may be used to show that the above definitions yield the statistical Saha equation

\[ \frac{k_r}{k_d} = \frac{[H_2]}{[H]^2} = \frac{Q_{H_2}}{Q_H^2 Q_T} \] (5)

for the thermalization of the continuum. For the results reported here, we assume that the system is in equilibrium. Corrections for non-LTE conditions are estimated to be small. The calculations use an energy sudden approximation which was tested for He+H+H by comparing with coupled states calculations [8]. Results from the two methods showed good agreement at temperatures greater than 600 K. The calculations also assume that the atoms are distinguishable which should be a good approximation at the high temperatures under consideration and is consistent with classical calculations. The BKMP2 [9] potential energy
surface (PES) was employed for the calculations. Previous quasiclassical calculations by Esposito and Capitelli [10] found that the BKMP2 PES gave very similar results compared to the LSTH PES [11] over the same temperature range considered in the present work.

Figure 1 shows the results of the present calculations together with the three TBR rate constants considered in the study of Turk et al. [1]. The present results are smaller than those of Flower and Harris [3] and Palla et al. [4] over the entire temperature range shown. These curves are both based on the experimental data of Jacobs et al. [2] as discussed above. Compared to the Palla et al. curve, we find good agreement with the extrapolation at high temperatures but poor agreement at low temperatures. We see the opposite effect when compared to the Abel et al. curve. The present calculations produce a much flatter temperature dependence than the other three curves. This flat temperature dependence is in good agreement with the quasiclassical results of Esposito and Capitelli [10] which were also computed using the BKMP2 PES. The magnitude of the present results agree with those of Esposito and Capitelli to within a factor of 2 over the entire temperature range shown. They also agree to within a factor of 2 with Jacobs et al. [2] and Orel [7]. Therefore, the factor of $\sim 100$ uncertainty which was introduced by the various extrapolations is estimated to be reduced to a factor of $\sim 2$ when the present results are used.

The results of the present calculations may be conveniently expressed by the function

$$k_r = 6 \times 10^{-32} T^{-1/4} + 2 \times 10^{-31} T^{-1/2}$$

using the same units as in Figure 1. This expression is virtually identical to the calculations for $T = 600 - 6000$ K and not too different at the endpoints of the range shown in the figure. This analytic function should be reliable for temperatures required by the hydrodynamics simulations. Based on previous simulations [1] it is expected that the gravitational collapse will produce a gas distribution which is somewhere in between the spherical distribution obtained using the Abel et al. [6] rate constant and the bar-shaped distribution obtained using the Palla et al. [4] rate constant.

It is noteworthy that recent numerical simulations of gravitational fragmentation by Clark et al. [12] adopted a TBR rate constant which was in between that of Palla et al. [4]
and Abel et al. [6]. This rate constant was due to Glover [13] who used CID rate constants of Martin et al. [14] together with the fitted equilibrium constant of Flower and Harris [3] which as noted above is 4 times too large when $T < 2000$ K. It is recommended that future astrophysical simulations of gravitational collapse employ the revised equilibrium and TBR rate constants accordingly.

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Figure 1: TBR rate constant for H+H+H. The present results show a much flatter temperature dependence than the curves of Flower and Harris [3], Palla et al [4], and Abel et al. [6].
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