Journal of Atomic, Molecular, Condensate & Nano Physics
Vol. 6, No. 3, pp. 179–186, 2015
ISSN 2349-2716 (online); 2349-6088 (print)
Published by RGN Publications

http://www.rgnpublications.com

Quantum Mechanical Rate Coefficient of Formation of HD Molecule at Ultracold Temperatures: Its Importance in Interstellar Cooling

Research Article

Ranga Santosh and Subhas Ghosal*

Department of Chemistry, Birla Institute of Technology and Science Pilani, Hyderabad Campus, Hyderabad 500 078, India

***Corresponding author:** ghosal@hyderabad.bits-pilani.ac.in

Abstract. Molecular hydrogen and its isotope HD acted as one of the most important interstellar coolants in the primordial gas medium. In this paper, we present accurate *time-independent quantum mechanical* (TIQM) rate coefficients of formation of ultracold HD molecules by $D + H_2(v, j) \rightarrow HD(v', j') + H$ reaction at very low collision energy. State resolved integral cross sections between different rotational (j) and vibrational (v) levels and corresponding Boltzmann-averaged thermal rate coefficients are computed between temperature $T = 10^{-8}$ K-10 K. We found the exponential decrease of the rate coefficients with reducing temperature following Arrhenius' empirical equation is not valid at ultracold temperature limit. At lower temperatures, the rate coefficients become independent of temperature (constant) and Wigner's threshold laws are obeyed. Since cooling of the primordial gases lead to the formation of the first structures of the universe, inclusion of the accurate low-temperature rate coefficients will lead to improved modeling for the evolution of the early universe.

Keywords. Ultracold HD; Reaction dynamics

PACS. 07.10.-h; 03.65.-w

Received: June 13, 2015 **Accepted:** October 25, 2015

1. Introduction

In the quest to understand our origin, scientists have explored many different possibilities (based on experiments and observations) to understand the evolution process of the early universe. In this journey, all scientific evidences route through the basic understanding of various atomic and molecular collisions at different external conditions. According to the popularly known big-bang theory [1], the universe was extremely hot and dense at the beginning and matter was present in the form of nucleons, e.g. quarks, electrons, protons, neutrons etc. As the universe expanded and temperature reduced gradually, the collisions between the neucleons lead to the formation of light atoms such as H, D, He, Li, He^+, Li^+ etc. [2]. Later, reactions among these lighter atoms and ions further resulted in the formation of small molecules such as H_2, HD, LiH, H_2^+, H_2D, H_2D^+ etc. Heavier atoms such as carbon, oxygen, iron and corresponding molecules were produced much later through nucleosynthesis.

From the observational evidences of the cosmic background radiation, it is believed that the temperature of the interstellar medium gradually decreased mainly because of the rapid collisions among the atoms, ions and molecules in the medium. When a fast moving atom or ion collided with a molecule most of the kinetic energy was absorbed by the molecule leading to either formation of a new species or excitation of the molecule to high rotational or vibrational quantum states. Later, as the excited molecule spontaneously relax to the ground state, energy was released in the form of electromagnetic radiation, most of which got dissipated in the surroundings. In this cycle, a significant amount of kinetic energy got converted into background radiation leading to slowing down of the atoms and molecules which resulted an overall cooling of the interstellar medium. This process of radiative cooling is particularly efficient for molecules with large number of closely spaced rotational and vibrational states for relaxation. Thus, light molecules like H_2, HD etc acted as very efficient interstellar coolant in the evolution process of the early universe [3].

The efficiency of cooling, i.e. how much energy is lost per second at a particular temperature, is defined as cooling functions for a particular species [4]. To calculate the cooling functions, the knowledge of state-to-state rate coefficients is required from very high to low temperature range for several chemical reactions leading to formation and destruction of that species. The radiative cooling functions are later coupled with the fractional abundance of that particular species to obtain the overall evolution of the interstellar medium.

In this paper, we present the accurate quantum mechanical rate coefficients of $D+H_2(v,j) \rightarrow HD(v',j')+H$ reaction at ultracold temperature limit. This reaction has been extensively studied experimentally and theoretically at higher temperatures by several research groups [5, 6, 7] but no experimental measurement has been done below 173 K. The rate coefficients at lower temperatures has been extrapolated using empirical formulas given by Arrhenius equations. But the Arrhenius theory, which calculates the temperature dependence of the rate coefficients using the concept of activation energy, fails towards lower temperatures where quantum tunnelling effect dominates over the activation barrier [8]. Since the atoms and molecules of our interest can interact very efficiently at low temperatures, accurate quantum mechanical treatment is necessary to study this reaction at very low temperature. Inclusion of the accurate rate coefficients will lead to significant changes in the estimation of the cooling functions.

2. Theoretical Details

To study the $D + H_2$ reactive scattering dynamics, all collision arrangements are treated equivalently using hyperspherical coordinate system [9]. The time-independent quantum mechanical close coupling approach of Pack and Parker, Schatz *et al.* [10, 11] has been applied to calculate dynamical observables using a modified version of ABC reactive scattering code [12]. Hyperradial equations are solved based on log-derivative method of Manolopoulos [13] from $\rho = \rho_{\min}$ to $\rho_{\max}$ with small enough integration step to represent the fine curvatures of the *potential energy surface* (PES). At each collision energy scattering matrix S (E) is extracted from the final log derivative matrix Y $(\rho_{\max})$ by applying the asymptotic boundary conditions [10]. Detail theoretical methodology have been presented in refs. [14, 7], we briefly discuss the essential components here.

The total integral cross sections for the transitions from an initial rovibrational state of the entrance arrangement (labeled by the quantum numbers $\lambda v j$) to a final state $(\lambda' v' j')$, can be expressed in terms of the corresponding S-matrix elements as

$$\sigma_{\lambda v j \to \lambda' v' j'}(E_{\lambda v j}) = \frac{\pi}{k^2_{\lambda v j}} \sum_{J=0}^{\infty} \left(\frac{2J+1}{2j+1}\right) \sum_{\ell=|J-j|}^{|J+j|} \sum_{\ell'=|J-j'|}^{|J+j'|} \left|\delta_{\lambda\lambda'}\delta_{jj'}\delta_{\ell\ell'}\delta_{vv'} - S^J_{\lambda\lambda' jj' \ell\ell' vv'}\right|^2, \qquad (2.1)$$

where the total angular momentum quantum number J is represented as $\vec{J} = \vec{\ell} + \vec{j}$, and ℓ and ℓ' are the initial and final orbital angular momentum quantum numbers, respectively. The wave number corresponding to the incoming channel is defined as $k_{\lambda v j} = \sqrt{2\mu(E - \varepsilon_{\lambda v j})}/\hbar$, where E is the total energy, $\varepsilon_{\lambda v j}$ is the energy of the initial rovibrational state, and μ is the atom-molecule reduced mass. The kinetic energy in the initial channel is given by $E_{\lambda v j} = (E - \varepsilon_{\lambda v j}) = \hbar^2 k^2_{\lambda v j}/2\mu$. The state-selected rate coefficients for the inelastic process are obtained by averaging the cross sections over a Boltzmann velocity distribution of the colliding species at a particular temperature T.

$$\mathrm{R}(T) = \frac{\sqrt{8k_B T/\pi\mu}}{(k_B T)^2} \int_0^{\infty} E_{\lambda v j} e^{\frac{-E_{\lambda v j}}{k_B T}} \sigma_{\lambda v j \to \lambda' v' j'}(E_{\lambda v j}) dE\,. \qquad (2.2)$$

At room temperature or higher, because of large collision energies, many rovibrational channels contribute to the overall reaction cross sections. Also contributions from higher total angular momentum (J) needs to be considered. But, in the ultracold temperature limit, due to very low collision energies, only s-waves, with orbital angular momentum $\ell = 0$ contribute to the total collision cross sections. Thus, the sums over J and ℓ in Eq. (2.1) are reduced to one term only. While this is an enormous simplification, there are also great difficulties specific to the ultracold temperature regime. At ultracold temperature limit, the translational kinetic energy between the colliding species becomes vanishingly small and the corresponding de Broglie wave length becomes extremely large. Thus, due to predominating quantum mechanical wave behavior, the colliding species can interact from very large internuclear distance. This leads to the crucial dependence of the reaction kinematics on the long range part of the interaction potential. We have performed several test calculations, which were rather expensive despite the current advances in computational power, and present here the results based on optimized numerical parameters.

We have used the BKMP2 PES [15], for our present work. The PES includes long range van der Waals dispersion coefficients and accurate enough to correctly represent the extremely sensitive ultracold collisions. Converged results were obtained with optimized numerical parameters: $E_{\max} = 4.75$ eV, $\rho_{\max} = 50$ a.u. and $\Delta\rho = 0.002$ a.u.

3. Results and Discussion

In a previous paper [7], we have studied the collisions of vibrationally excited H_2 molecules on $D + H_2(v, j = 0) \rightarrow HD(v', j') + H$ reaction only considering s-wave contribution ($J = j = \ell = 0$) at ultra-low collision energies. In this paper, we present accurate reaction cross sections and rate coefficients including contribution from higher partial waves ($\ell > 0$). Because of the slowly varying nature of the long range interaction potential, higher partial waves starts to contribute even for collision energy below 1 Kelvin. For $D + H_2$ reaction, we found reactive collisions upto $J = 0, 1, 2$ (s, p and d waves) contribute within this collision energy range. The state selected total reaction cross sections are shown in Figure 1 as function of collision energy. Initial rovibrational states of H_2 are indicated in the legends. Here, the sum is extended over all open inelastic channels, i.e., the final states of $H_2(j', v' \neq v)$ and open $HD(j', v')$ channels. The contributions from individual s, p and d partial waves to the overall reaction cross sections are shown in Figure 2. For collisions with $D + H_2$ ($v = 0, j = 0$) only three channels in the product arrangement are open $HD(v' = 0, j' = 0, 1, 2)$, thus the curve corresponding to $v = 0$, $j = 0$ in Figure 1 represent the total reaction cross sections for $D + H_2(0, 0)$ collisions.

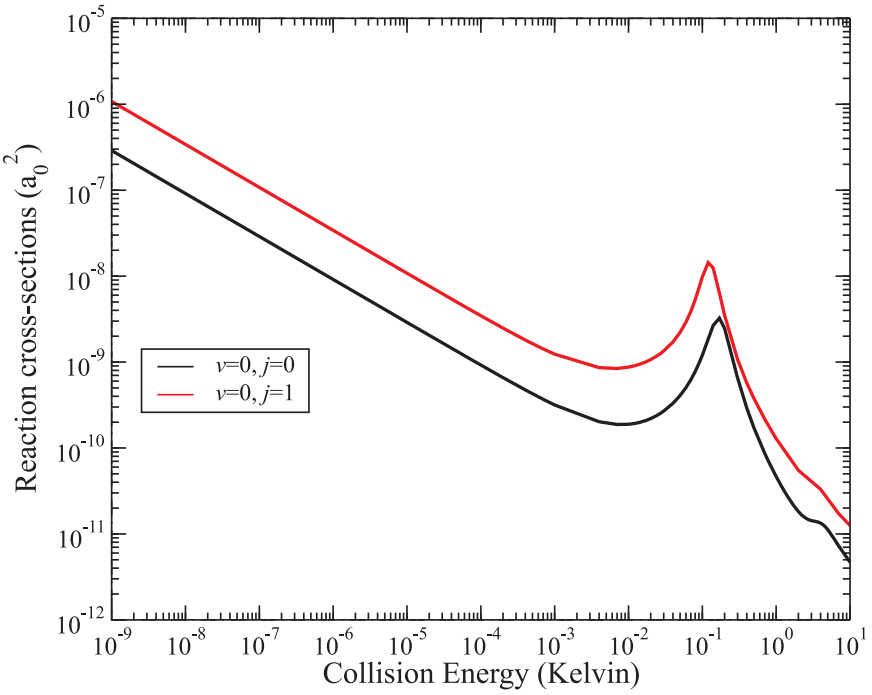

Figure 1. Collision energy dependence of reaction cross sections of $D + H_2$ (v, j) collisions. Initial rovibrational states are indicated in the legend. Note that for $v = 0$, $j = 0$, all open channels leads to the formation of product $HD(v', j') + H$, whereas, for $v = 0$, $j = 1$, quenching cross sections to $D + H_2$ $(v = 0, j = 0)$ state is also included.

It is evident from Figure 1, even with vanishingly small collision energies, the reaction can proceed through quantum mechanical tunnelling. The reaction cross sections increase as the collision energy is decreased to very low collision energies. This is because the atoms and molecules have diffuse boundary (due to large de Broglie wave length) at low collision energies and the effective range of interaction increases with decreasing average velocity of the colliding species. Therefore, the scattering dynamics at ultra-low collision energies are governed by Wigner's threshold laws [16]. According to the threshold law, the reaction cross sections, σ_{inel} is proportional to $E_{\rm coll}^{\ell-1/2}$. This simple power law behavior produces straight lines at ultra low collision energies in the logarithmic graphs of Figure 1. There are not much enhancement in the reaction cross sections due to rotational excitation ($j = 1$) as shown in Figure 1. This is expected as the barrier suppression effect still predominates over the small increase in collision energies due to rotational excitation. Thus, we restrict the rotational excitation only up to j=1 for the current study.

At low collision energies, we distinguish two very different regimes in the collision energy dependence of the reaction cross sections: very low collision energies ($E_{\rm coll} \leq 1$ mK) where, the Wigner's threshold laws [16] are obeyed, followed by a gradual transition into the barrier dominated regime at higher collision energies. Below $\sim 1\mu$ Kelvin ($\sim 10^{-9}$eV) contribution to the reaction cross sections are purely due to the s-wave ($\ell = 0$) collisions, but as collision energy increase higher partial waves $\ell = 1, 2, \ldots$ starts to contribute. Thus, there are significant increase in the reaction cross sections for collision energies above ~0.001 Kelvin compared to our previous s-wave only calculations [7].

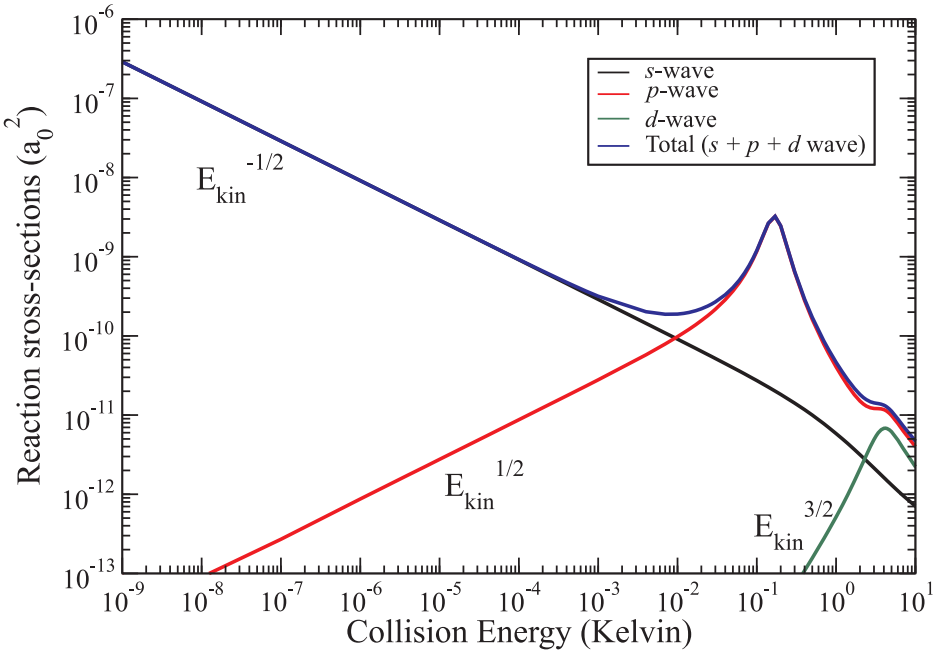

Figure 2. s, p and d wave contribution to the total inelastic cross section of D+H_2 ($v = 1, j = 0$) collisions. Low collision energy behavior according to Wigner's threshold laws [16] are verified for individual partial waves.

Finally, we present the state-selected rate coefficients in Figure 3. Rate coefficients are obtained by averaging the reactive cross sections over a Boltzmann velocity distribution at a particular temperature T according to Eq. (2.2). On averaging the reactive cross sections over the narrow velocity distribution at ultracold temperature limit, the rate coefficients attains a constant value, which is in accord to the Wigner's threshold laws [16]. The sharp increase in the cross sections for $v = 0$, $j = 0$ initial state leads to a broad hump in the rate coefficients around $T = 0.001$-0.1 K.

The temperature dependence of the rate coefficients at ultracold temperature limit behaves in complete disagreement with the familiar Arrhenius law ($K_{\mathrm{Arrh}}(T) = A\exp(-B/T)$, where A and B constant) as shown in Figure 3. Arrhenius extrapolation of the available high temperature rate coefficients from ref. [5] leads to vanishingly small values at ultracold temperature limit. Inclusion of near constant rate coefficients for temperatures ≤ 10 K will lead to significant change in the low temperature cooling function of HD molecule which can be used for better modelling of the astrophysical processes of the early universe. Calculations on corrected cooling functions are currently under progress.

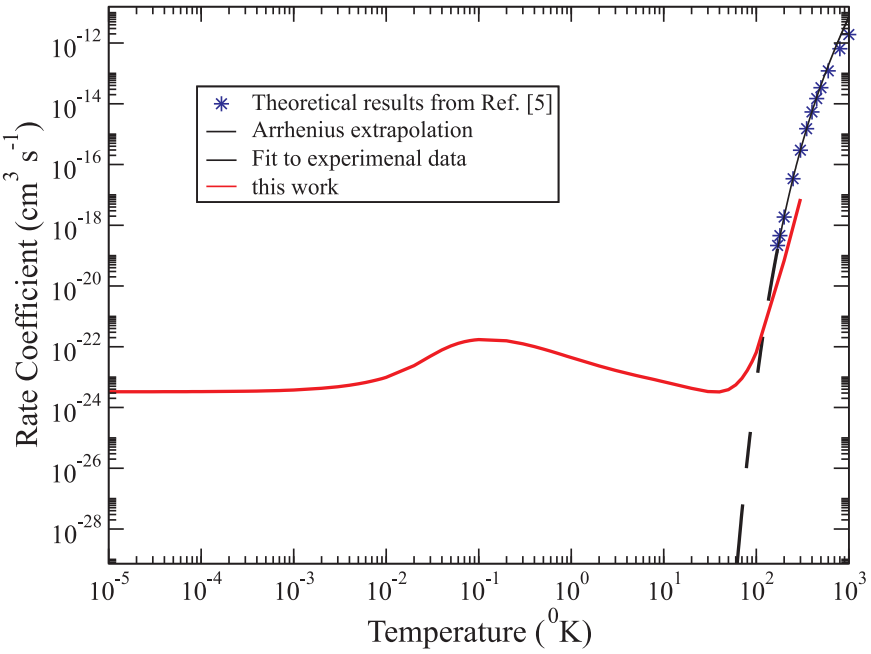

Figure 3. Temperature dependence of the rate coefficients of D + $H_2(v = 0, j = 0)$ → HD + H reaction. High temperature experimental measurements and theoretical calculations and Arrhenius extrapolation from ref. [5] are also shown for comparison.

4. Summary and conclusion

In this paper, we have performed accurate close-coupling calculations for $D + H_2(v, j) \rightarrow HD(v', j') + H$ reactive scattering dynamics for temperature below 1 Kelvin. In ultracold temperature limit, the rate coefficients do not follow Arrhenius equation rather it become independent of temperature. This is in accord to Wigner's threshold laws [16] of quantum reactive scattering. Since HD molecule is one of the very important interstellar coolant, accurate

low temperature rate coefficients of this reaction may help to incorporate appropriate corrections in astrophysical modeling.

Acknowledgements

This study is supported by Grant No. SR/FT/CS-129/2011 from Department of Science and Technology (DST), New Delhi, India. RS thanks CSIR India for fellowship

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed equally and significantly in writing this article. All the authors read and approved the final manuscript.

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