# HD + *ortho-*/*para-*H$_2$ rotational energy transfer non-reactive scattering at low astrophysical temperatures: 2 K ≲ T ≲ 300 K

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Abstract. State-resolved integral cross sections and corresponding thermal rate coefficients are computed for the HD + *ortho-*/*para-*H$_2$ rotational energy transfer collision at low temperatures of astrophysical interest: 2 K ≲ T ≲ 300 K. A recent original full-dimensional H$_2$-H$_2$ potential energy surface (PES) was adopted and appropriately modified for the current non-symmetrical four-atomic system.

1 Introduction

One of the most important few-body systems in the field of atomic and molecular physics is, probably, the non-reactive scattering problem between two hydrogen molecules, i.e. H$_2$+H$_2$. The four-atomic symmetrical system, H$_2$+H$_2$, represents the two simplest and lightest identical diatomic molecules. In astrophysical applications H$_2$ can play a significant role, since it is the most abundant chemical species in the universe's molecular clouds. Consequently, the H$_2$-H$_2$ interaction and collisions have always attracted significant theoretical and experimental attention. The system has been considered in many previous works, see for example [1–5]. After H$_2$, the second most abundant primordial molecule is HD - deuterated hydrogen, where D is the hydrogen isotope ^{2}H - deuterium. Just like the H$_2$ + H$_2$ collision, the HD + H$_2$ energy transfer collision is also of significant importance in the astrophysics of the early Universe and in the modeling of pre-galactic clouds and planetary atmospheres. The HD molecule plays an important role in the chemistry of the interstellar medium [6] as well as the rotational and possibly vibrational energy transfer collisions between H$_2$ molecules. Further, collisions between H$_2$ and HD are important for the cooling of primordial gas and in the formation of first stars [7, 8]. In order to compute elastic/in-elastic scattering outputs, one needs to construct a PES between colliding molecules first. The HD-H$_2$ potential can be obtained from the initial H$_2$-H$_2$ potential by shifting the original H$_2$ molecule's center of mass (c.m.) to the coordinate of the c.m. of the HD molecule. Once the exchange symmetry is broken in H$_2$+H$_2$ by replacing the H by the D atom in one H$_2$ one has the new HD-H$_2$ PES. Thereby, one can derive the HD-H$_2$ PES from the original H$_2$-H$_2$ PES employing all parts of the full HD-H$_2$ interaction including the HD's dipole moment. Using the HD-H$_2$ PES derived from the H$_2$-H$_2$ PES of Hinde [4] we carry out full quantum calculations for collisions of rotationally excited HD and H$_2$ molecules, i.e. the process:

$$\text{HD}(j_1) + \text{H}_2(j_2) \rightarrow \text{HD}(j_1') + \text{H}_2(j_2'). \tag{1}$$
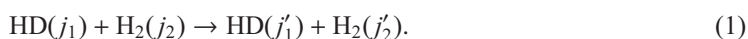
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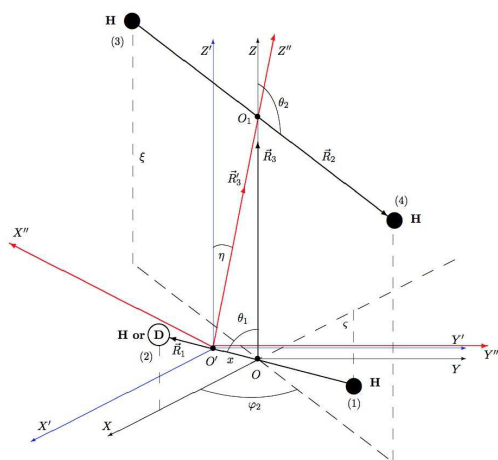
Figure 1. (Color online) Four-atomic system (1, 2, 3, 4) or H-D-H-H is shown together with its *few-body Jacobi coordinates* $\{\vec{R}_1, \vec{R}_2, \vec{R}_3\}$. The original Cartesian coordinate system is $OXYZ$. The center of mass of the original H_2 molecule lies at point O. $O'X'Y'Z'$ is a system which was shifted in parallel from the original system, O' lies in the center of mass of the actual HD molecule. The close-coupling equations are solved using the space-fixed coordinate system $O'X''Y''Z''$, which is obtained by rotation over the axis OY'. The vector $\vec{R}'_3$ connects the center of masses of the HD and H_2 molecules. HD is the first molecule with a rotational constant $B_e(1)=44.7$ cm^{-1} and quantum angular momentum of j_1, H_2 is the second molecule with rotational constant of $B_e(2)=60.8$ cm^{-1} and uses momentum j_2 in the system; $R_1 = 0.7631$ Å and $R_2 = 0.7668$ Å are fixed interatomic distances in each hydrogen molecule HD and H_2 respectively.

The scattering cross sections and their corresponding thermal rate coefficients are computed using a non-reactive quantum-mechanical close-coupling approach.

2 Quantum-mechanical method and results

1. Dynamical equations. The details of the quantum-mechanical approach used in the current work has been described in few previous papers. See, for example, preprint [9] and references therein. Briefly, a four-atomic Schrödinger equation is numerically solved in the framework of the quantum-mechanical close-coupling approach [2]. The HD and H_2 molecules are treated as linear rigid rotors. In our calculations, with the use of two PESs from works [3, 4] the bond length was fixed at 1.449 a.u. or 0.7668 Å for the H_2 molecule and 1.442 a.u. for HD which is 0.7631 Å. The Schrödinger equation for the (12) + (34) collision in the c.m. frame, where (12) and (34) are diatomic molecules is:

$$\left[\frac{\hat{P}^2_{\vec{R}_3}}{2\mathcal{M}_{12}} + \frac{\hat{L}^2_{\hat{R}_1}}{2\mu_1 R_1^2} + \frac{\hat{L}^2_{\hat{R}_2}}{2\mu_2 R_2^2} + V(R_1, \hat{R}_1, R_2, \hat{R}_2, \vec{R}_3) - E \right] \Psi(\hat{R}_1, \hat{R}_2, \vec{R}_3) = 0. \tag{2}$$

Here $\hat{P}_{\vec{R}_3}$ is the momentum operator of the kinetic energy of the collision, $\vec{R}_3$ is the collision coordinate, whereas $\vec{R}_1$ and $\vec{R}_2$ are relative vectors between atoms in the two diatomic molecules, and $\hat{L}_{\hat{R}_{1(2)}}$ are the quantum-mechanical rotation operators of the rigid rotors, μ_1 and μ_2 are the reduced masses of the HD and H_2 molecules and $\mathcal{M}_{12}$ is the reduced mass of the two molecules. Also, $V(R_1, \hat{R}_1, R_2, \hat{R}_2, \vec{R}_3)$ is the PES of the four-atomic system (1234), E is the total energy in the c.m. system, and $\hat{R}_{1(2)}$ are the angles of orientation for rotors (12) and (34), respectively, it is shown in Fig. 1. The use and modification of the original H_2-H_2 PESs [3, 4], $V(\vec{R}_1, \vec{R}_2, \vec{R}_3)$, is discussed below and in greater detail in [9, 10]. The cross sections for excitation from HD(j_1, m_1)+$H_2(j_2, m_2)$ to HD($j'_1 m'_1$)+$H_2(j'_2 m'_2)$ are summed over the final angular momentum projections ($m'_1 m'_2$) and averaged over the initial projections ($m_1 m_2$) of the HD and H_2 molecules of angular momenta j_1 and j_2: $\sigma(j'_1, j'_2; j_1 j_2, \varepsilon) = \pi/[(2j_1 + 1)(2j_2 + 1)k_{\alpha\alpha'}] \sum_{J j_{12} j'_{12} LL'} (2J + 1)|\delta_{\alpha\alpha'} - S^J_{\alpha\alpha'}(E)|^2$. The kinetic energy is $\varepsilon = E - B_1 j_1(j_1 + 1) - B_2 j_2(j_2 + 1)$, where $B_1 = 44.7$ cm^{-1} and $B_2 = 60.8$ cm^{-1} are the rotational
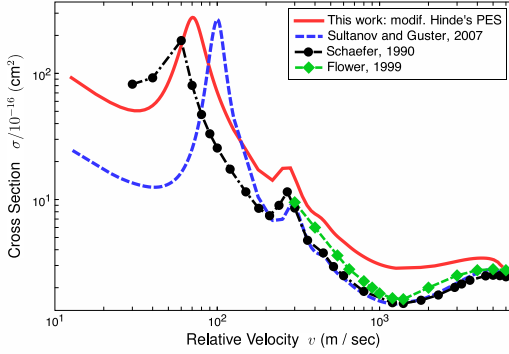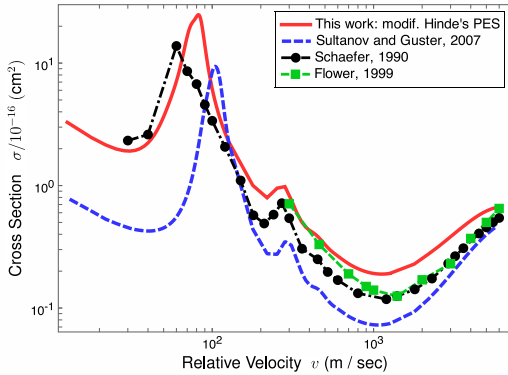
Figure 2. (Color online) The total cross section of the HD(1) + H$_2$(0) → HD(0) + H$_2$(0) inelastic rotational energy transfer collision. The numbers in parentheses are the rotational quantum numbers of the two-atomic molecules.
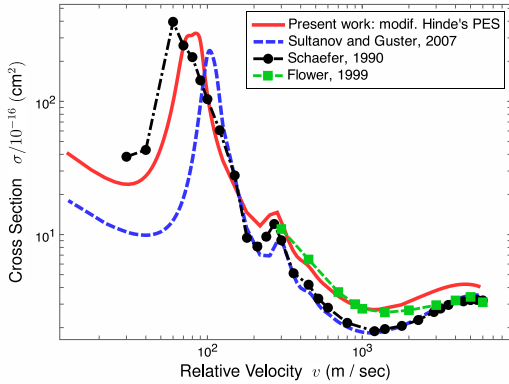
Figure 3. (Color online) The total cross section of the HD(2) + H$_2$(0) → HD(1) + H$_2$(0) inelastic rotational energy transfer collision. The numbers in parentheses are the rotational quantum numbers of the two-atomic molecules.

constants of rigid rotors (12) and (34) respectively. Further, J is total angular momenta of the four-atomic system, $\alpha \equiv (j_1 j_2 j_{12} L)$, where $j_1 + j_2 = j_{12}$ and $j_{12} + L = J$, $k_{\alpha\alpha'} = \sqrt{2\mathcal{M}_{12}(E + E_\alpha - E_{\alpha'})}$ is the channel wavenumber and $E_{\alpha(\alpha')}$ are rotational channel energies.

2. Interaction potentials. Based on the Born-Oppenheimer idea [11] any quantum-mechanical, semi-classical or, say, quasi-classical trajectory treatment of the HD+H$_2$, D$_2$+HD or, say, D$_2$+D$_2$ four-atomic systems should begin with consideration of the original H$_2$-H$_2$ PES. The full six-dimensional function comprises a symmetrical surface over the OZ coordinate axis. In spherical coordinates the surface can be described by six variables: R_1, θ_1, R_2, θ_2, R_3, and φ_2 [4]. The variables are shown in Fig. 1. In work [3] an H$_2$-H$_2$ potential was formulated in a Cartesian coordinate system. In both works the H$_2$-H$_2$ potential was derived in the framework of the Born-Oppenheimer model [11] and can basically be considered as a symmetrical interaction field. When considering non-reactive scattering problems with participation of hydrogen molecules, one needs to solve the Schrödinger Eq. (2) with the H$_2$-H$_2$ potential $V(\vec{R}_1, \vec{R}_2, \vec{R}_3)$. The solution/propagation runs over the $\vec{R}_3$ Jacobi vector, which can be directed over the OZ axis, this is shown in Fig. 1. Therefore, in the case of the symmetrical H$_2$+H$_2$ and D$_2$+D$_2$ collisions, one can use the original H$_2$-H$_2$ PES as it is, i.e. without transformations. However, in the case of the non-symmetrical (symmetry-broken) HD+H2/D2 or HD+HD scattering systems, one should also apply the original H$_2$-H$_2$ interaction field or PES, but in this case the propagation (solution) of the Schrödinger equation should run over the corrected Jacobi vector $\vec{R}'_3$ which is directed over the new $O'Z''$ axis. This is shown in Fig. 1. In the current work, and in the preprint [9], we used two modified potentials from the papers [3, 4].

Figure 4. (Color online) The total cross section of the HD(2) + H_2(0) → HD(0) + H_2(0) inelastic rotational energy transfer collision. The numbers in parentheses are the rotational quantum numbers of the two-atomic molecules.
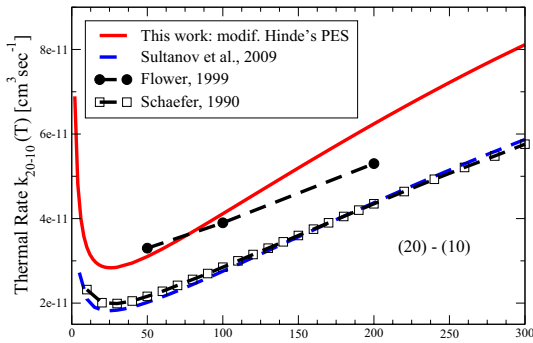
Figure 5. (Color online) The rotational de-excitation thermal rate coefficient $k_{ij \to i'j'}$ (T) for the following collision: HD(2) + H_2(0) → HD(1) + H_2(0).
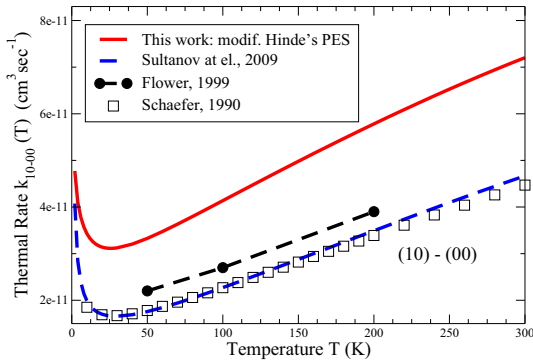
Figure 6. (Color online) The rotational de-excitation thermal rate coefficient $k_{ij \to i'j'}$ (T) for the following collision: HD(1) + H_2(0) → HD(0) + H_2(0).

3. Results. In order to solve the Schrödinger Eq. (2) the MOLSCAT program [12] has been used in our calculations. Because the HD+H_2 total rotational energy transfer cross sections have shape resonances at the low energy sector, a large number of energy points were needed. We used up to 250 energy points in each computation for each specific rotational transition in the HD and H_2 molecules considered. Convergence was obtained for the integral cross sections, $\sigma(j_1', j_2'; j_1 j_2, \varepsilon)$, with respect to the variation of the variables utilized in all considered collisions at different energies. For the intermolecular distance R_3, we used from R_{3min} = 3.0 a.u. to R_{3max} = 30.0 a.u. Our new rotational energy transfer integral cross sections are shown only for three different quantum-state transitions in the HD and H_2 molecules. Specifically, HD(1) + H_2(0) → HD(0) + H_2(0), HD(2) + H_2(0) → HD(1) + H_2(0) and HD(2) + H_2(0) → HD(0) + H_2(0) are presented in figures 2, 3 and 4. However, in

the recent preprint [9] more results for different rotational transitions in the HD and H$_2$ molecules are available together with the important thermal rate coefficients at different temperatures: $k_{j_1 j_2 \to j_1' j_2'}(T)$ [9]. The shape resonances in the low velocity region are reproduced, which are important in the cooling of the astrophysical media [6, 7]. Two thermal rate coefficients $k_{j_1 j_2 \to j_1' j_2'}(T)$ [9] are presented in figures 5 and 6 as examples. Again, one can find more results in [9]. The new results are compared with the older quantum-dynamical calculations of Schaefer [7] and Flower [8] . The computational results from the older work [10] are also shown. These data have been obtained by using a PES obtained from a modification of the BMKP H$_2$-H$_2$ PES [3]. One can see that the new cross sections obtained with the Hinde's PES have the same structure and shape, but also have substantially larger ($\sim 60\%$) values at medium energies ($v \gtrsim 200$ m/sec) when compared with the results obtained from the modified BMKP PES [3] and the older result from Schaefer's calculations [7]. The cross sections from Ref. [8] are available only for higher collision velocities, i.e. $v \geq 300$ m/s. In summary, state-resolved close-coupling quantum-mechanical calculations for rotational de-excitation cross-sections and corresponding thermal rate coefficients of the HD+o-/p-H$_2$ collisions are computed using a linear rigid rotor model for the HD and H$_2$ molecules. The symmetrical H$_2$-H$_2$ PES of Ref. [4] has been appropriately adopted for the current non-symmetrical HD+H$_2$ system by appropriate translation and rotation. These geometrical operations lead to a new set of angle variables θ_1', θ_2' and φ_2' for the Jacobi few-body coordinates, a new length of the intermolecular distance $\vec{R}_3'$ and, as a result, to a new HD-H$_2$ PES [9]. The new results can be used for subsequent consideration (at different astrophysical conditions) the astrophysical HD-cooling function, $\Lambda_{\text{HD}}(T)$, which is important in the astrophysics of the early universe [6]. Also, the substantially larger cross sections and rates in HD+o-/p-H$_2$ found in the current work and in [9] with the use of the modified Hinde PES are consistent with previous results for H$_2$+H$_2$ [13]. It has also been shown [13, 14] that full-dimensional dynamics which employ the Hinde PES [4] generally provide fairly good agreement with experiments for the low-lying vibrational states of H$_2$. Therefore, it can be recommended that the new results presented in [13, 14] for H$_2$+H$_2$, and in [9] for HD+H$_2$, which employ the Hinde PES, can be adopted in the astrophysical models.

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