A comparative study of the low energy HD+o-/p-H2 rotational excitation/de-excitation collisions and elastic scattering

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The Diep and Johnson (DJ) H2-H2 potential energy surface (PES) obtained from the first principles [P. Diep, K. Johnson, J. Chem. Phys. 113, 3480 (2000); 114, 222 (2000)], has been adjusted through appropriate rotation of the three-dimensional coordinate system and applied to low-temperature (T < 300 K) HD+o-/p-H2 collisions of astrophysical interest. A non-reactive quantum mechanical close-coupling method is used to carry out the calculation for the total rotational state-to-state cross sections $\sigma_{j_1,j_2 \rightarrow j'_1,j'_2}(\epsilon)$ and corresponding thermal rate coefficients $k_{j_1,j_2 \rightarrow j'_1,j'_2}(T)$. A rather satisfactory agreement has been obtained between our results computed with the modified DJ PES and with the newer H4 PES [A.I. Boothroyd, P.G. Martin, W.J. Keogh, M.J. Peterson, J. Chem. Phys. 116, 666 (2002)], which is also applied in this work. A comparative study with previous results is presented and discussed. Significant differences have been obtained for few specific rotational transitions in the H2/HD molecules between our results and previous calculations. The low temperature data for $k_{j_1,j_2 \rightarrow j'_1,j'_2}(T)$ calculated in this work can be used in a future application such as a new computation of the HD cooling function of primordial gas, which is important in the astrophysics of the early Universe.

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I. INTRODUCTION

The simplest quantum-mechanical scattering problem, that between two hydrogen molecules, has been a formidable challenge to chemists and physicists working in this area. This is because the elastic and inelastic H2+H2 scattering have all the complications of a complex molecular scattering process like rotational and vibrational excitations and de-excitations. Many theoretical and experimental methods have been developed and used for the study of these processes. Additionally, there has been great interest in the study of HD+H2 scattering. Although, this system bears some similarity with H2+H2, the identical system symmetry is broken here and hence many aspects of the theoretical formulation can be tested in the system under different symmetry conditions.

The PESs of H2+H2 and HD-H2 are basically the same six-dimensional functions. The fact follows from a general theoretical point of view and the Born-Oppenheimer model. However, from an intuitive physical point of view, the two collisions should have different scattering output. This is because the H2 and HD molecules have fairly different rotational constants and rotational-vibrational spectrum. They have different internal symmetries and dipole moments. Collisional properties of these systems are expected to be highly sensitive to dipole moments. Further, the HD-H2 PES can be derived from H2+H2 by adjusting the coordinate of the center of mass of the HD molecule. Once the symmetry is broken in H2+H2 by replacing the H by the D atom in one H2 molecule one can obtain the HD-H2 PES. The new potential has all parts of the full HD-H2 interaction including HD’s dipole moment. However, in a case when a PES is formulated for fixed interatomic coordinates between the two hydrogen atoms in the H2-H2 system, it would be difficult to extract the PES of HD-H2, because the position of the HD center of mass is different from that of H2. In this work we apply a rotational method for calculation of the HD-H2 PES from that of H2-H2. The method is based on a rotation of the three-dimensional space from the body-fixed H2-H2 coordinate system to appropriately adjust the HD molecule center of mass.

The hydrogen molecule plays an important role in many areas of astrophysics. For example, the interstellar medium (ISM) cooling process is associated with the energy loss after inelastic collisions of the particles. These processes convert the kinetic energy of ISM’s particles to their internal energies: for instance, in the case of molecules to their internal energy of rotational-vibrational degrees of freedom. Therefore, in order to accurately model the thermal balance and kinetics of ISM one needs accurate state-to-state cross sections and thermal rate constants. Theoretical state-resolved treatment requires precise PES of H2-H2, and a reliable dynamical method for H2+H2/HD collision. However, on the other hand, experimental measurements of these cross sections is a very difficult technical problem. Unfortu-
nately, up to now no reliable experiments are available on these collision processes, which have important astrophysical applications. Moreover, different calculations with various H$_2$-H$_2$ PESs showed rather different results for important H$_2$+H$_2$ thermal rate coefficients.

The possible importance of the HD cooling in ISM was first noted in 1972 by Dalgarno and McCray. Because of the special properties of HD this molecule is even more effective cooler than H$_2$. This happens at low temperatures $T < 100$ $K$, where the cooling function of HD becomes $\sim 15$ times larger than the H$_2$ cooling function. As we mentioned in the previous paragraph, to carry out calculation of the cooling function one needs to know precise cross sections and thermal rate coefficients of the rotational-vibrational energy transfer collisions. That is why there is a constant interest to reliable quantum-mechanical computation of different rotational-vibrational atom-molecular energy transfer collision cross sections and corresponding thermal rate coefficients.

A realistic full-dimensional ab initio PES for the H$_2$-H$_2$ system was first constructed by Schwenke and that potential was widely used in a variety of methods and computation techniques. Flower used Schwenke’s H$_2$-H$_2$ PES in a study of H$_2$-HD collision. Later on, new extensive studies of the H$_2$-H$_2$ system by Diep and Johnson (DJ) and Boothroyd et al. (BMKP) have produced refined PES for the H$_2$-H$_2$ system. These PESs have been used in several different calculations. However, in our previous work we found that in the case of low energy H$_2$+H$_2$ collision these PESs provide different results for some specific state-to-state resolved cross sections. The difference may be up to an order of magnitude. This fact was also confirmed in work. The BMKP PES, probably, needs future improvements, because the DJ PES gives better agreement with existing experiments for H$_2$+H$_2$ than the BMKP potential.

Nonetheless, as a first trial Sultanov et al. applied the BMKP PES to the low-energy HD+H$_2$ collisions after appropriate modification. When the results of these calculations were compared with prior studies, a relatively good agreement was found with Schaefer’s results. At the same time substantial differences with the newer data obtained by Flower was noted. Therefore, in the light of these circumstances, it would be useful to apply another modern H$_2$-H$_2$ PES to HD-H$_2$ collisions. The DJ potential was formulated specifically for the symmetric H$_2$-H$_2$ system when distances between hydrogen atoms are fixed at a specific equilibrium value in each H$_2$ molecule. In this paper we provide the first calculation describing collisions of rotationally excited H$_2$ and HD molecules using the DJ PES. We also provide a comparison with our previous calculations with the BMKP PES, which is a global six-dimensional surface.

In Sec. II we briefly outline the quantum-mechanical close-coupling approach and our method to convert the symmetric DJ PES to be appropriate for calculations of the HD+H$_2$ system. We represent results for selected state-to-state cross sections and thermal rate coefficients for rotational excitation/de-excitation of HD in low-energy collisions with $\alpha$/-$\beta$-H$_2$ in Sec. III. Finally, in Sec. IV we present a brief summary of our findings and conclusion.

II. COMPUTATIONAL METHOD

A. Dynamical equations

The Schrödinger equation for the (12)+(34) collision in the center-of-mass frame, where 1, 2, 3 and 4 are atoms and (12) and (34) are diatomic molecules modeled by linear rigid rotors, is:

$$\left[ \frac{P_{\tilde{R}_3}^2}{2M_{12}} + \frac{L_{\tilde{R}_1}^2}{2\mu_1 \tilde{R}_1^2} + \frac{L_{\tilde{R}_2}^2}{2\mu_2 \tilde{R}_2^2} + V(\tilde{R}_1, \tilde{R}_2, \tilde{R}_3) - E \right] \Psi(\tilde{R}_1, \tilde{R}_2, \tilde{R}_3) = 0, \quad (1)$$

where $P_{\tilde{R}_3}$ is the momentum operator of the kinetic energy of collision, $\tilde{R}_3$ is the collision coordinate, whereas $\tilde{R}_1$ and $\tilde{R}_2$ are relative vectors between atoms in the two diatomic molecules as shown in the Fig. and $L_{\tilde{R}_{1(2)}}$ are the quantum-mechanical rotation operators of the rigid rotors. Here, $M_{12} \equiv [(m_1 + m_2)(m_3 + m_4)]/[(m_1 + m_2 + m_3 + m_4)]$ is the reduced mass of the two diatomic molecules (12) and (34) and $\mu_{1(2)} \equiv [m_1(m_3 + m_2(4)]/[(m_1(3) + m_2(4))]$ are reduced masses of the two molecules. The vectors $\tilde{R}_{1(2)}$ are the angles of orientation of rotors (12) and (34), respectively; $V(\tilde{R}_1, \tilde{R}_2, \tilde{R}_3)$ is the PES for the four-atomic system (1234), and $E$ is the total energy in the center-of-mass system. The linear rigid-rotor model used in this calculation was already applied in some previous studies. For the considered range of kinetic energies of astrophysical interest the model is quite justified.

The eigenfunctions of the operators $L_{\tilde{R}_{1(2)}}$ in Eq. (1) are simple spherical harmonics $Y_{j_m}(\hat{r})$. To solve this equation the following angular-momentum expansion is used:

$$\Psi(\tilde{R}_1, \tilde{R}_2, \tilde{R}_3) = \sum_{J M_{1j_2j_1j_3}L} \frac{U^{JM}_{j_1j_2j_3j_4} L(\tilde{R}_3)}{R_3} \times \phi^{JM}_{j_1j_2j_3j_4} L(\tilde{R}_1, \tilde{R}_2, \tilde{R}_3) \quad (2)$$

where $U^{JM}_{j_1j_2j_3j_4} L(\tilde{R}_3)$ are unknown coordinate functions, $J$ is total angular momentum quantum number of the (1234) system and $M$ is its projection onto the space fixed $Z$ axis, and channel functions are the following:

$$\phi^{JM}_{j_1j_2j_3j_4} L(\tilde{R}_1, \tilde{R}_2, \tilde{R}_3) = \sum_{\tilde{m}_1\tilde{m}_2\tilde{m}_3\tilde{m}_4} C_{j_1\tilde{m}_1\tilde{m}_2j_2\tilde{m}_2}^{J M_{j_3j_4\tilde{m}_3\tilde{m}_4}} \times Y_{j_1\tilde{m}_1}(\tilde{R}_1)Y_{j_2\tilde{m}_2}(\tilde{R}_2)Y_{L\tilde{m}_3}(\tilde{R}_3), \quad (3)$$
unknown radial functions in Fig. 1. Quantum-mechanical momenta \( \vec{R} \) over the corresponding Jacobi coordinates between \( \vec{R}_1 \) and \( \vec{R}_2 \). The vector \( \vec{R}_3 \) connects the center of masses of the HD and H\(_2\) molecules and is directed over the axis OZ, \( \theta_1 \) is the angle between \( \vec{R}_1 \) and \( \vec{R}_3 \), \( \theta_2 \) is the angle between \( \vec{R}_2 \) and \( \vec{R}_3 \), \( \varphi_1 \) is the torsional angle, \( j_1, j_2, L \) are quantum angular momenta over the corresponding Jacobi coordinates \( \vec{R}_1, \vec{R}_2, \vec{R}_3 \).

where \( j_1 + j_2 = j_{12}, j_{12} + L = J, m_1, m_2, m_{12} \) and \( m \) are projections of \( j_1, j_2, j_{12} \) and \( L \), respectively. The \( C' \)'s are the appropriate Clebsch-Gordan coefficients. The quantum-mechanical momenta \( j_1, j_2 \) and \( L \) over corresponding Jacobi vectors \( \vec{R}_1, \vec{R}_2 \) and \( \vec{R}_3 \) are also shown in Fig. 1.

Upon substitution of Eq. (2) into Eq. (1), one obtains a set of coupled second order differential equations for the unknown radial functions \( U^{JM}_{\alpha'}(R_3) \):\(^{33,40}\)

\[
\left( \frac{d^2}{dR_3^2} - \frac{L(L+1)}{R_3^2} + k_\alpha^2 \right) U^{JM}_{\alpha'}(R_3) = 2M_{12} \sum_{\alpha'} \int \langle \phi^{JM}_{\alpha'}(\vec{R}_1, \vec{R}_2, \vec{R}_3)|V(\vec{R}_1, \vec{R}_2, \vec{R}_3)\rangle \phi^{JM}_{\alpha'}(\vec{R}_1, \vec{R}_2, \vec{R}_3) > U^{JM}_{\alpha'}(R_3) d\vec{R}_1 d\vec{R}_2 d\vec{R}_3,\quad (4)
\]

where \( \alpha \equiv (j_{12}j_{12}L) \). We apply the hybrid modified log-derivative-Airy propagator in the general-purpose scattering program MOLSCAT \(^{31}\) to solve the coupled radial Eq. (4).

The log-derivative matrix is propagated to large intermolecular distances \( R_3 \), since all experimentally observable quantum information about the collision is contained in the asymptotic behavior of functions \( U^{JM}_{\alpha'}(R_3 \rightarrow \infty) \). The numerical results are matched to the known asymptotic solution to derive the scattering \( S \)-matrix \( S'_{\alpha'\alpha} \):

\[
U^{J}_{\alpha} \sim \delta_{\alpha\alpha'} e^{-i(k_\alpha R_3 - l\pi/2)} - \sqrt{k_{\alpha'} \alpha'} S^{J}_{\alpha\alpha'} \times e^{-i(k_{\alpha'} R_3 - l'\pi/2)},\quad (5)
\]

where \( k_{\alpha\alpha'} = \sqrt{2M_{12}(E + E_{\alpha} - E_{\alpha'})} \) is the channel wave number, \( E_{\alpha(\alpha')} \) are rotational channel energies for \( \alpha \) and \( \alpha' \). The method was used for each partial wave until a converged cross section was obtained. It was verified that the results are converged with respect to the number of partial waves as well as the matching radius, \( R_{3\text{max}} \), for all channels included in our calculation. The cross sections for rotational excitation and relaxation can be obtained directly from the \( S \)-matrix. In particular the cross sections for excitation from \( j_1j_2 \rightarrow j_1'j_2' \) summed over the final \( m_1'm_2' \) and averaged over the initial \( m_1m_2 \) are given by

\[
\sigma(j_1', j_2'; j_1j_2,\epsilon) = \pi \sum_{j_1j_2j_1',j_2'} (2J + 1) \frac{|\delta_{\alpha\alpha'} - S^J(j_1', j_2'; j_1j_2L; j_1j_2j_1', j_2, j_1, j_2, L; E)|^2}{(2j_1 + 1)(2j_2 + 1)k_{\alpha\alpha'}}\quad (6)
\]

The relative kinetic energy of the two molecules in the center of mass frame is:

\[
\epsilon = E - B_1j_1(j_1 + 1) - B_2j_2(j_2 + 1),\quad (7)
\]

where \( B_{1(2)} \) are the rotation constants of rigid rotors (12) and (34), respectively, of total angular momentum \( j_{1(2)} \). The relationship between the rotational thermal-rate coefficient \( k_{j_1j_2\rightarrow j_1'j_2'}(T) \) at temperature \( T \) and the corresponding cross section \( \sigma_{j_1j_2\rightarrow j_1'j_2'}(\epsilon) \), can be obtained through the following weighted average: \(^{32}\)

\[
k_{j_1j_2\rightarrow j_1'j_2'}(T) = \frac{1}{(k_B T)^2} \int \frac{8k_B T}{\pi M_{12}} \int_\epsilon \sigma_{j_1j_2\rightarrow j_1'j_2'}(\epsilon) e^{-\epsilon/k_B T} d\epsilon,\quad (8)
\]

where \( k_B \) is Boltzman constant and \( \epsilon_s \) is the minimum relative kinetic energy of the two molecules for the levels \( j_1 \) and \( j_2 \) to become accessible.

B. The BMKP \( H_2-H_2 \) PES

The BMKP PES \(^{31}\), is a global six-dimensional potential energy surface for two hydrogen molecules. It was especially constructed to represent the whole interaction region of the chemical reaction dynamics of the four-atomic system and to provide an accurate van der Waals well. In the six-dimensional conformation space of the four-atomic system the PES forms a complicated three-dimensional hyper surface \(^{31}\). To compute the distances between the four atoms \( R_1, R_2 \) and \( R_3 \), the BMKP PES uses Cartesian coordinates. Therefore it was necessary to convert spherical coordinates used in the close-coupling method \(^{31}\) to the corresponding Cartesian coordinates and compute the distances between the four atoms followed by calculation of the PES \(^{37,38}\). Without the loss of generality the procedure used a specifically oriented coordinate system \( OXYZ \). First we introduce the Jacobi coordinates \( \{\vec{R}_1, \vec{R}_2, \vec{R}_3\} \) and the radius-vectors of all four atoms in the space-fixed coordinate system \( OXYZ \): \( \{\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4\} \) (not shown in Fig. 1). As in Ref. \(^{33}\) we apply the following procedure: the center of mass of the HD molecule is put at the origin of the coordinate system \( OXYZ \), and the \( \vec{R}_3 \) is directed to
center of mass of the H$_2$ molecule along the OZ axis, as shown in Fig. 1. Then $\vec{R}_3 = \{R_3, \Theta_3 = 0, \Phi_3 = 0\}$, with $\Theta_3$ and $\Phi_3$ the polar and azimuthal angles, $\vec{R}_1 = \vec{r}_1 - \vec{r}_2$, $\vec{R}_2 = \vec{r}_4 - \vec{r}_3$, $\vec{r}_1 = \xi \vec{R}_1$ and $\vec{r}_2 = (1 - \xi) \vec{R}_1$, where $\xi = m_2/(m_1 + m_2)$.

Next, without the loss of generality, we can adopt the OXYZ system in such a way, that the HD interatomic vector $\vec{R}_1$ lies on the XOZ plane. Then the angle variables of $\vec{R}_1$ and $\vec{R}_2$ are: $R_1 = \{\Theta_1, \Phi_1 = \pi\}$ and $\vec{R}_2 = \{\Theta_2, \Phi_2\}$ respectively. One can see, that the Cartesian coordinates of the atoms of the HD molecule are:

$$\vec{r}_1 = \{x_1 = \xi R_1 \sin \Theta_1, y_1 = 0, z_1 = \xi R_1 \cos \Theta_1\},$$

$$\vec{r}_2 = \{x_2 = -(1 - \xi) R_1 \sin \Theta_1, y_2 = 0, z_2 = -(1 - \xi) R_1 \cos \Theta_1\}.$$

Defining $\zeta = m_4/(m_3 + m_4)$, we have

$$\vec{r}_3 = \vec{R}_3 - (1 - \zeta) \vec{R}_2,$$

$$\vec{r}_4 = \vec{R}_3 + \zeta \vec{R}_2,$$

and the corresponding Cartesian coordinates:

$$\begin{align*}
\vec{r}_3 &= \{x_3 = -(1 - \zeta) R_2 \sin \Theta_2 \cos \Phi_2, \\
y_3 &= -(1 - \zeta) R_2 \sin \Theta_2 \sin \Phi_2, \\
z_3 &= R_3 - (1 - \zeta) R_2 \cos \Theta_2\},
\end{align*}$$

$$\begin{align*}
\vec{r}_4 &= \{x_4 = \zeta R_2 \sin \Theta_2 \cos \Phi_2, \\
y_4 &= \zeta R_2 \sin \Theta_2 \sin \Phi_2, \\
z_4 &= R_3 + \zeta R_2 \cos \Theta_2\}. 
\end{align*}$$

C. The Modified Diep and Johnson H$_2$-H$_2$ potential

Below we briefly present our method to convert the symmetric DJ H$_2$-H$_2$ PES to be suitable for the non-symmetric system HD+H$_2$. The method is based on a mathematical transformation technique, i.e. a geometrical rotation of the three-dimensional (3D) space and the corresponding space-fixed coordinate system OXYZ, as shown in Fig. 2. It is more convenient here to use a slightly different from Fig. 1 orientation of the coordinate system OXYZ: now the center of mass of the H$_2$ molecule is set at the origin of the space-fixed OXYZ, and $\vec{R}_3$ ($\vec{R}_3$) is directed to the center of mass of H$_2$ (HD).

The few-body system (1234) can be characterized by four radius-vectors: {\(r_1, r_2, r_3, r_4\)}, or alternatively by so-called three Jacobi vectors: {\(\vec{R}_1, \vec{R}_2, \vec{R}_3\)}. Usually the second option is more convenient for describing the quantum-mechanical few-body systems. Next, the initial geometry of the system is taken in such a way that the Jacobi vector $\vec{R}_3$ connects the center of masses of the two molecules and is directed over the OZ axis. We can also choose OXYZ in such a manner that the Jacobi vector $\vec{R}_2$ lies in the X-Z plane. Finally, the vector $\vec{R}_1$ can be directed anywhere. Then the spherical coordinates of the Jacobi vectors are: $\vec{R}_1 = (R_1, \phi_1, \phi_1)$, $\vec{R}_2 = (R_2, \phi_2, 0)$, and $\vec{R}_3 = (R_3, 0, 0)$. Thus the 4-body system H$_2$-H$_2$/HD can be fully determined with the use of six variables. However, the DJ PES has been prepared for the rigid monomer model of H$_2$-H$_2$\footnote{\(1\)}, so actually we have only four active variables in this consideration: $R_3, \theta_1, \phi_1$, and $\phi_1$. The DJ PES has been prepared as the following function for the distance $R_3$ between two H$_2$ molecules, two polar angles $\theta_1(2)$ and one torsional angle $\phi_1$:

$$V(R_3, \theta_1, \phi_1) = \sum_{l_1,l_2,l} V_{l_1,l_2,l}(R_3) G_{l_1,l_2,l}(\theta_1, \theta_2, \phi_1),$$

where the angular functions $G_{l_1,l_2,l}$ are\footnote{\(1\)}:

$$\begin{align*}
G_{000}(\theta_1, \theta_2, \phi_1) &= 1, \\
G_{200}(\theta_1, \theta_2, \phi_1) &= \frac{5}{2} (3 \cos^2 \theta_1 - 1), \\
G_{022}(\theta_1, \theta_2, \phi_1) &= \frac{5}{2} (3 \cos^2 \theta_2 - 1), \\
G_{222}(\theta_1, \theta_2, \phi_1) &= \frac{45}{4\sqrt{70}} [2(3 \cos^2 \theta_1 - 1) \\
&+ 3 \cos^2 \theta_2 - 1 - 16 \sin \theta_1 \cos \theta_1 \sin \theta_2 \\
&\times \cos \theta_2 \cos \phi_1 + \sin^2 \phi_1 \sin^2 \theta_2 \cos(2\phi_1)].
\end{align*}$$

The coordinate function $V_{l_1,l_2,l}(R_3)$ has been tabulated in work\footnote{\(1\)}.
First we start with the original DJ PES of Eqs. (15)-(19). Then we replace one hydrogen atom “H” with a deuterium atom “D”. Thus we break the symmetry by shifting the center of mass of one H₂ molecule to another point, that is from O₁H₂ to O₁HD as shown in Fig. 2. We also need to take into account the difference between the number of rotational states in H₂+H₂ and HD+H₂. The length of the vector x is x = |R₂|/6. Now we rotate the OXYZ coordinate system around the OY axis in such a way that the new OZ' axis goes through the point O₁HD. The OY' axis and the old OY axis are parallel, and the angle of this small rotation is η, see Fig. 2.

This transformation converts the initial Jacobi vectors in OXYZ: \( \vec{R}_1 = \{R_1, \theta_1, \phi_1\} \), \( \vec{R}_2 = \{R_2, \theta_2, 0\} \) and \( \vec{R}_3 = \{R_3, 0, 0\} \) to the corresponding Jacobi vectors with new coordinates in the new O’X’Y’Z’: \( \vec{R}'_1 = \{R'_1, \theta'_1, \phi'_1\} \), \( \vec{R}'_2 = \{R'_2, \theta'_2, 0\} \) and \( \vec{R}'_3 = \{R'_3, 0, 0\} \). As a result of this simple procedure we obtain a new PES, namely:

\[
V^\text{HD}_{\text{D,J}}(R_3, \theta_1, \theta_2, \phi_1) \rightarrow V^\text{HD}_{\text{D,J}}(R'_3, \theta'_1, \theta'_2, \phi'_1). \quad (20)
\]

It is quite obvious, that the rotation does not affect the coordinate function \( V_{l_1,l_2,l}(R_3) \) in Eq. (15). Note, in a previous calculation of low energy collision between monodeuterated ammonia NH₂D and a helium atom, a somewhat similar spatial rotational-translational procedure has been applied to the original PES of the NH₃-He system.\[5\]

Next, any rotation of the 3D OXYZ coordinate system can be represented by Euler angles, i.e. \( \{\alpha, \beta, \gamma\} \). In this work we choose the following Euler angles: \( \alpha = 0, \beta = \eta, \gamma = 0 \). To calculate the value of the rotational angle η in Fig. 2 we can consider the internal triangle \( \Delta OHD/OO'H_2 \), which is shown in Fig. 2. The angle η is determined from the following formula:

\[
\cot \eta = \frac{(R'_3 + x \sin \theta'_2)}{x \cos \theta'_2}. \quad (21)
\]

The derivation of (21) can be expressed as follows. First, the angles of the triangle \( \Delta OHD/OO'H_2 \) satisfy the following equation \( (\pi - \theta_2) + \eta + \theta'_2 = \pi \) or \( \theta_2 = \eta + \theta'_2 \). Secondly, based on the law of sines for \( \Delta OHD/OO'H_2 \):

\[
\frac{x}{\sin \eta} = \frac{R}{\sin \theta'_2} = \frac{R'}{\sin \psi}, \quad (22)
\]

where \( \psi = \pi - \theta_2 \). Because \( \sin \psi = \cos \theta_2 \) we have:

\[
\frac{x}{\sin \eta} = \frac{R}{\sin \theta'_2} = \frac{R'}{\cos \theta_2}, \quad (23)
\]

and finally:

\[
\frac{\cos(\eta + \theta'_2)}{\sin \eta} = \frac{R'}{x}, \quad (24)
\]

from which one can directly obtain the expression (21).

In such a way the rotation of the coordinate system from OXY to O’X’Y’Z’ makes a corresponding transformation of the coordinates of the atoms in the 4-body system and the distance between two molecules. One has the following relations among old and new variables\[45\]:

\[
\cos(\theta_1) = \cos(\theta'_1) \cos(\eta) - \sin(\theta'_1) \sin(\eta) \cos(\phi'_1) \quad (25)
\]

\[
\cos(\theta_2) = \cos(\theta'_2) \cos(\eta) - \sin(\theta'_2) \sin(\eta) \cos(\phi'_1) \quad (26)
\]

\[
\cos(\phi_{12}) = \cos(\phi'_1) \cos(\eta) + \sin(\eta) \sin(\phi'_1) \quad (27)
\]

\[
R_3 = \sqrt{x^2 + R'_3^2 - 2xR'_3 \cos(\theta'_2)}. \quad (28)
\]

In the calculation of HD+H₂ with the DJ PES one has to use new coordinates \( \theta'_1, \theta'_2, \phi'_1, R'_3 \). However, the potential (15) has been expressed through the old H₂-H₂ variables, hence it is to be transformed to new variables using Eqs. (20) – (23).

III. NUMERICAL RESULTS

Results for the low energy HD+o-/p-H₂ elastic scattering cross-sections and few selected quantum-mechanical rotational transitions together with the corresponding results from previous studies\[37,38\] are presented below. The cross sections are also compared with the corresponding results from\[5,21\]. Additionally, we compare our results for the thermal rate coefficients\[5\] with previous calculations\[5,21\]. The results for the low energy elastic scattering cross sections cannot be compared with other theoretical/experimental data. To the best of our knowledge such calculations do not exist.

A. Elastic scattering

In Fig. 3 we show the present elastic scattering cross sections for HD+o-/p-H₂ collisions at low and ultra-low energies calculated using three different potentials: the BMKP potential of Sec. IIIC, the modified DJ potential of Sec. IIIC and the original DJ potential appropriate for the H₂-H₂ system. In each cross section there is a prominent resonance. In Fig. 3 although the shapes of three cross sections are similar to each other the resonance peak and the position of the resonance differ significantly when we use the original DJ potential without the modifications described in the Sec. IIIC. This is because the original, symmetrical DJ potential\[5\] does not have all the asymmetrical features of the HD+H₂ interaction. Moreover, these features are of crucial importance for HD+H₂ scattering. In Table III we show the elastic cross sections \( \sigma_{el}(\epsilon) \) for a few selected energies calculated with the three potentials. We also include in Table III the results for scattering lengths \( a_0 \)'s. As can be seen from Fig. 3 and Table III we have obtained extremely good agreement between our calculations with the BMKP and with the modified DJ PESs. For the considered range of the kinetic energies we obtained full numerical convergence, for instance, the total angular momentum J.
TABLE I. The elastic scattering cross sections $\sigma_{el}$ (10^{-16}cm^2) at selected relative kinetic energies $\epsilon$ (cm^{-1}) and corresponding scattering lengths $a_{scatt}$ (10^{-6}cm) in the $\alpha-/p$-H$_2$ + HD $\rightarrow$ $\alpha-/p$-H$_2$ + HD low energy collisions calculated with three different potentials: modified DJ PES from Sec. II C and original BMKP$^{21}$ and DJ$^{24}$ PESs. Numbers in parentheses are powers of 10.

| $\epsilon$ (cm^{-1}) | $\sigma_{el}$ $\times$ 10^{-16} (cm^2) | $p$-H$_2$ + HD |
|---------------------|---------------------------------|----------------|
|                     | mod. DJ                        | BMKP            | DJ              | mod. DJ                        | BMKP            | DJ              |
| 4.0(-5)             | 348.61                         | 380.70          | 375.29          | 408.68                         | 380.02          | 375.87          |
| 5.0(-5)             | 348.61                         | 380.70          | 375.29          | 408.68                         | 380.02          | 375.87          |
| 1.0(-4)             | 348.59                         | 380.67          | 375.27          | 409.96                         | 380.00          | 375.86          |
| 1.0(-2)             | 406.4                          | 378.1           | 372.5           | 406.6                          | 378.5           | 373.0           |
| 1.0(-1)             | 386.4                          | 362.2           | 355.3           | 386.6                          | 362.5           | 355.8           |
| 3.0(-1)             | 385.0                          | 359.0           | 1705.0          | 385.0                          | 359.1           | 2039.8          |
| 4.0(-1)             | 467.3                          | 418.9           | 516.26          | 466.1                          | 416.9           | 529.0           |
| 6.0(-1)             | 1641.2                         | 1577.6          | 433.8           | 1653.2                         | 1611.5          | 437.0           |
| 1.0                 | 592.0                          | 520.1           | 419.3           | 593.3                          | 522.6           | 421.0           |
| 5.0                 | 504.4                          | 492.9           | 501.5           | 504.4                          | 492.8           | 501.8           |
| 10                  | 331.1                          | 310.7           | 353.3           | 331.1                          | 310.6           | 353.1           |
| 100                 | 87.6                           | 84.6            | 93.2            | 87.6                           | 84.6            | 93.1            |

Scattering length: $a_{scatt}$ x 10^{-6} (cm)

| $\epsilon$ $\rightarrow$ 0.0 | 5.27 | 5.50 | 5.46 | 5.70 | 5.50 | 5.47 |

was used up to the maximum value $J_{\text{max}} = 12$ in this calculation.

B. Non-elastic channels

The main goal of the present study is not to obtain results for every possible transition cross section in the HD+H$_2$ collision, but rather to demonstrate how the appropriately undertaken 3D rotation of the symmetrical surface of the H$_2$ - H$_2$ system could be adapted for collision of the H$_2$ and HD molecules. We carry out calculations for a fairly wide region of the collision energies, i.e. from 3 K to up to 300 K. This temperature interval is relevant for future calculations of the important HD-cooling function$^{24}$. Here we compute few transition cross sections in which we noticed substantial differences between our results obtained with the two different PESs from Refs. 1 and 31 and also between our results and the data from previous studies$^{21}$.

In Figs. 4 to 8 we show these results for a few selected state-to-state HD+$\alpha-/p$-H$_2$ integral cross sections. The results have been calculated with two different potentials, specifically, with the BMKP PES$^{21}$ of Sec. II B and the modified DJ PES of Sec. II C. When possible we compare our results with existing previous calculations for the state-selected total cross sections and thermal rate coefficients. It is necessary to mention that the original DJ surface$^{24}$ cannot be correctly used for the non-elastic or transition channel calculations, i.e. for the rotational state transitions in an HD+H$_2$ collision. If the original, unmodified DJ potential is applied one can get extremely low numbers ($\sim 10^{-35}$) for the HD+H$_2$ rotational state-to-state probabilities and cross sections. That is why it was necessary to undertake the geometrical modifications to the DJ surface described in Sec. II C. We obtained a fairly good agreement between our calculations with the use of the two PESs. Besides some qualitative differences in the state-resolved total cross sections the overall behavior of the cross section $\sigma_{j_1j_2\rightarrow j'_1j'_2}(v)$ was found identical, where $v$ is the relative velocity of the two molecules. However we obtained substantial differences between our $\sigma_{j_1j_2\rightarrow j'_1j'_2}(v)$ cross sections and corresponding data from Ref. 5.

In Fig. 4 we plot the total cross sections for the rotational transitions (02) - (20) and (13) - (11). The notation of the rotational quantum numbers can be understood by comparison to the following equations:

$$\text{HD}(0) + \text{H}_2(2) \rightarrow \text{HD}(2) + \text{H}_2(0),$$

$$\text{HD}(1) + \text{H}_2(3) \rightarrow \text{HD}(1) + \text{H}_2(1),$$

where the numbers in parenthesis denote rotational quantum numbers $j_1$, $j_2$ etc.. On the upper plot it is seen that while the two results of this study are in fairly good agreement between each other we obtain substantial disagreements with the result of Ref. 5. The same is true in the lower plot, although the behavior of these cross sections has a common character.

In Fig. 5 we show the cross sections for rotational transitions in HD+H$_2$ for the BMKP and the modified DJ PESs for the processes HD(1) + H$_2$(3) $\rightarrow$ HD(0) + H$_2$(1), and HD(1) + H$_2$(3) $\rightarrow$ HD(2) + H$_2$(1). The corresponding results from Ref. 5 are also shown. We again obtain a fairly good agreement between our results computed with the BMKP and the modified DJ PESs, however, differing significantly from the corresponding Schaefer result$^{22}$. Unfortunately we cannot compare these cross sections with the results of the calculation by Flower$^{23}$, in which a different H$_2$-H$_2$ potential from$^{30}$ was used. This is because Flower’s data includes results mostly for
FIG. 3. (Color online) Elastic scattering total cross sections for HD+α-H₂ (upper panel) and HD+α-H₂ (lower panel) at different kinetic energies with the BMKP PES of Sec. II C and the modified DJ PES and the original DJ PES.

FIG. 4. (Color online) Total cross sections for transition (02) → (20) and (13) → (11), i.e. HD(0)+H₂(2) → HD(2)+H₂(0) (upper panel) and HD(1)+H₂(3) → HD(1)+H₂(1) (lower panel) for different velocities \( v \). Present calculations with the BMKP PES and modified DJ PESs are compared with those of Ref. [5].

the thermal rate coefficients. However, within the next subsection in Table II we compare our few selected rotational state-resolved thermal rate coefficients with the corresponding results from Refs. [5] and [21].

From the astrophysical point of view, perhaps, one needs only precise rotational and in some rare cases vibrational state-to-state thermal rate coefficients \( k_{j_1,j_2 \rightarrow j'_1,j'_2}(T) \) in \( H₂+H₂, \) HD+H₂ etc. These quantities are less sensitive to interaction potentials. However, the overall behavior of all possible state-selected cross sections should be very important for calculation of the thermal rates as seen in Fig. 3. It appears that the cross sections are much more sensitive to the PESs used in the calculations. Hence it is useful and even probably important in some specific cases to compare the cross sections from various calculations where different PESs have been used.

Further, Figs. 4 and 5 exhibit our results for the state-to-state rotational cross sections in transitions HD(2) + H₂(1) → HD(0) + H₂(1) and HD(1) + H₂(2) → HD(2) + H₂(0) in transitions HD(2) + H₂(0) → HD(0) + H₂(0) and HD(2) + H₂(0) → HD(1) + H₂(0), respectively. We obtained fairly good agreement between our own results. Additionally, in these rotational transitions fairly good agreement with the corresponding cross sections from Ref. [5] has also been obtained. Finally, Fig. 5 shows our integral cross section for the transition HD(0) + H₂(2) → HD(2) + H₂(0). This process is also interesting, because the transition occurs in the two molecules simultaneously. We would like to name such processes as double-transition processes.

C. Thermal rate coefficients

In Table II our rotational thermal rate coefficients \( k_{j_1,j_2 \rightarrow j'_1,j'_2}(T) \) are presented. In this paper we choose only three rotational double-transitions in the collision: (02)-(20), (12)-(20), and (20)-(02). These results were obtained from corresponding state-resolved integral cross sections \( \sigma_{j_1,j_2 \rightarrow j'_1,j'_2}(\epsilon) \) with the use of the expression (8). In a previous study [21], Flower compared his rotational transition thermal rate coefficients with the corresponding Schaefer data and found substantial differences between his results and results from Ref. [5] even at high temperatures. The point is that in these processes the transition occurs in the two molecules simultaneously. In such rotational transitions the probabilities and cross sections should be very sensitive to the interaction potential. Perhaps, because of this reason the results of Refs. [5] and [21] differ so dramatically for transitions like (02) - (20).
TABLE II. Results for three selected state-to-state rotational thermal rate coefficients $k_{j_1 j_2 \rightarrow j'_1 j'_2}(T)$ cm$^3$ s$^{-1}$ at various low temperatures $T$ (K) in the $p$-H$_2$(α) + HD(β) → $p$-H$_2$(α') + HD(β') collisions. Calculations with different PESs: the original BMKP PES and the new modified DJ potential from this work. The corresponding older data from other authors are also included in this table. Numbers in parentheses are powers of 10.

| $T$ (K) | $(02) \rightarrow (20)$ Rotational Thermal Rate Coefficients: $k_{j_1 j_2 \rightarrow j'_1 j'_2}(T)$ cm$^3$ s$^{-1}$ | $(12) \rightarrow (20)$ Rotational Thermal Rate Coefficients: $k_{j_1 j_2 \rightarrow j'_1 j'_2}(T)$ cm$^3$ s$^{-1}$ | $(20) \rightarrow (02)$ Rotational Thermal Rate Coefficients: $k_{j_1 j_2 \rightarrow j'_1 j'_2}(T)$ cm$^3$ s$^{-1}$ |
|---|---|---|---|
| | BMKP Mod. DJ Ref. 21 Ref. 5 BMKP Mod. DJ Ref. 21 Ref. 5 BMKP Mod. DJ Ref. 21 Ref. 5 |
| 10 | 1.18(-11) 6.38(-12) 7.21(-14) 6.35(-14) 9.32(-14) 1.06(-17) 3.43(-18) 2.53(-20) | 9.32(-14) 1.06(-17) 3.43(-18) 2.53(-20) | 2.16(-13) 3.21(-14) 4.36(-16) 2.17(-18) |
| 20 | 9.57(-12) 5.51(-12) 6.72(-15) 5.43(-14) 8.62(-14) 9.18(-14) 4.11(-15) 1.26(-17) | 8.62(-14) 9.18(-14) 4.11(-15) 1.26(-17) | 7.5(-14) 3.14(-13) 7.2(-13) |
| 30 | 9.05(-12) 5.40(-12) 7.40(-15) 5.34(-14) 9.53(-14) 8.80(-14) 4.48(-14) 1.13(-16) | 9.53(-14) 8.80(-14) 4.48(-14) 1.13(-16) | 2.8(-13) 9.15(-15) |
| 50 | 8.81(-12) 5.51(-12) 9.3(-13) 1.09(-14) 1.34(-13) 5.64(-14) 7.9(-14) 3.14(-13) | 8.81(-12) 5.51(-12) 9.3(-13) 1.09(-14) | 7.5(-14) 8.86(-16) |
| 70 | 8.83(-12) 5.68(-12) 1.70(-14) 1.52(-13) 6.06(-14) 1.21(-12) 7.38(-13) | 8.83(-12) 5.68(-12) 1.70(-14) 1.52(-13) | 2.8(-13) |
| 100 | 8.93(-12) 5.90(-12) 9.9(-13) 1.85(-13) 6.72(-14) 1.6(-13) 2.86(-13) 2.8(-13) | 8.93(-12) 5.90(-12) 9.9(-13) 1.85(-13) | 9.15(-15) |
| 200 | 9.17(-12) 6.29(-12) 1.1(-12) 3.25(-13) 8.78(-14) 4.3(-13) 7.31(-13) 6.0(-13) | 9.17(-12) 6.29(-12) 1.1(-12) 3.25(-13) | 7.69(-14) |
| 300 | 9.19(-12) 6.43(-12) 3.46(-13) 4.77(-13) 1.06(-13) 1.28(-12) 5.78(-12) 4.02(-12) | 9.19(-12) 6.43(-12) 3.46(-13) 4.77(-13) | 2.28(-13) |

In Table II we show our thermal rate coefficients for the processes HD(0) + H$_2$(2) → HD(2) + H$_2$(0), and HD(1) + H$_2$(2) → HD(2) + H$_2$(0), and those for HD(2) + H$_2$(0) → HD(0) + H$_2$(2). We present our results calculated with the BMKP PESs and with the modified DJ PESs. As before, our results computed with these two potentials are close to each other. However, one can see that our results and results from Refs. 5 and 21 differ significantly. This happens particularly at low temperatures, for instance from 10 K to 50 K. Finally in this section, for the process HD(2) + H$_2$(0) → HD(0) + H$_2$(2) the difference between our $k_{j_1 j_2 \rightarrow j'_1 j'_2}(T)$ and the results from Ref. 5 is about 3 orders of magnitude at T=10 K. The reason of this substantial deviation is not clear, although it might be a result of using different HD+H$_2$ potentials in the current computation and in Refs. 5 and 21, where...
the authors also used two different PESs and different quantum-mechanical methods. However, we would like to point out here that our results computed with two newer PESs\cite{31} are relatively close to each other.

\section*{D. Application of the detailed balance principle}

By using the time reversibility (reciprocity) principle one can obtain the detailed balance equation for the direct and reverse energy transfer processes or reactions\cite{32}.

In the case of the inelastic scattering \(a + b \rightleftharpoons a' + b'\) the detailed balance principle\cite{33} relates the direct \(a + b\) and the reverse \(a' + b'\) processes and their cross sections \(\sigma^{ab}_{aj_a \rightarrow j'_b j'_b}\) and \(\sigma^{a'b'}_{j'a' \rightarrow j_b j_b}\):

\[
(2j_a + 1)(2j_b + 1)p_{a\rightarrow b}\sigma^{ab}_{j_a j_b \rightarrow j'_a j'_b}(E) = (2j'_a + 1) \times (2j'_b + 1)p_{b\rightarrow a}\sigma^{a'b'}_{j'_a j'_b \rightarrow j_a j_b}(E). \tag{31}
\]

Here, \(E\) is the total energy, \(j_a(b)\) and \(j'_a(b)\) are the initial and final rotational quantum numbers, \(p_{a\rightarrow b}\) and \(p_{b\rightarrow a}\) are the initial and final relative momenta between \(a\) and \(b\) species, \(\sigma^{ab}_{j_a j_b \rightarrow j'_a j'_b}(E)\) and \(\sigma^{a'b'}_{j'_a j'_b \rightarrow j_a j_b}(E)\) are direct and reverse integral cross sections respectively. The same type of the relationship can be obtained for the thermal rate coefficients \(k_{j_1 j_2 \rightarrow j'_1 j'_2}(T)\). Let us rewrite Eq. (\ref{eq5}) in the terms of the total energy \(E\). Considering that the relative kinetic energy \(\epsilon\) between \(a\) and \(b\) is Eq. (\ref{eq7}), we compute the total energy from the lowest possible level between two channels. If it is associated with the second channel \(a' + b'\), i.e. \(j'_1 j'_2\) pair, the formula (\ref{eq8}) becomes:

\[
k^{a'b'}_{j'_1 j'_2 \rightarrow j_a j_b}(T) = \frac{1}{(k_B T)^2} \left( \frac{8k_B T}{\pi M_{12}} \right) \int_0^\infty \sigma_{j_1 j_2 \rightarrow j'_1 j'_2}(E) e^{-\frac{E}{k_B T}} dE. \tag{32}
\]

Here, \(\Delta E = [B_1 j_1 (j_1 + 1) + B_2 j_2 (j_2 + 1)] - [B_1 j'_1 (j'_1 + 1) + B_2 j'_2 (j'_2 + 1)]\) is the energy gap between the direct and reverse channels, and \(\epsilon = p^{a'b'} / M_{12}\) is the kinetic energy. Now, for the reverse channel the thermal rate coefficient is:

\[
k^{a'b'}_{j_1 j_2 \rightarrow j'_1 j'_2}(T) = \frac{1}{(k_B T)^2} \left( \frac{8k_B T}{\pi M_{12}} \right) \int_0^\infty \sigma_{j'_1 j'_2 \rightarrow j_1 j_2}(E) e^{-\frac{E}{k_B T}} dE, \tag{33}
\]

Comparing Eqs. (\ref{eq32}) and (\ref{eq33}) and taking into account Eq. (\ref{eq41}) we obtain the detailed balance formula for the thermal rate coefficients:

\[
(2j_1 + 1)(2j_2 + 1)k^{a'b'}_{j_1 j_2 \rightarrow j'_1 j'_2}(T) = (2j'_1 + 1)(2j'_2 + 1) \times k^{a'b'}_{j'_1 j'_2 \rightarrow j_1 j_2}(T)e^{\Delta E / k_B T}. \tag{34}
\]

The ratio \(R_{j_1 j_2 \rightarrow j'_1 j'_2}(T) = k^{a'b'}_{j_1 j_2 \rightarrow j'_1 j'_2}(T) / k^{a'b'}_{j'_1 j'_2 \rightarrow j_1 j_2}(T)\) is proportional to an exponent with the argument depending on \(\Delta E\). In this work we computed two direct-reverse processes in the HD + p-H₂ collisions, specifically:

\[
\text{HD}(0) + \text{H}_2(2) \rightarrow \text{HD}(2) + \text{H}_2(0), \tag{35}
\]

with \(\Delta E = 96.6 \text{ cm}^{-1}\). It would be useful to check how well the computed thermal rates (\ref{eq35}) in this work satisfy the detailed balance equation (\ref{eq34}). Fig. 9 represents these results. It is shown that all results are in a satisfactory agreement with each other.
References therein. The BMKP PES in failures. The fact was mentioned in Refs. 12 and 13 and the H model H the transformation of the 4-dimensional rigid monomer IV. CONCLUSION (34). Computation with the use of both potentials: the open circles are the values of the exponential function from the right side of Eq. 34. In this work a rotational method has been applied for collisions. Different low energy elastic and state-selected inelastic cross sections as well as the thermal rate coefficients for HD+H2 have been computed and compared with previous calculations, where available. The rotational energy transfer in HD+H2 is of importance for the thermodynamics of the ISM22. By now few and rather conflicting results are available for the low energy HD+H2 rotational energy transfer, see for examples28 and references therein. The BMKP PES21 has been already applied to HD+H2.27,28 However, this PES may have failures. The fact was mentioned in Refs. 12 and 13 and in. Therefore in this paper a new attempt has been undertaken to carry out alternative computational methods for HD+H2 collision. In case of the BMKP and DJ PESs the necessary steps for each potential have been described in Secs. 1113 and 1115 and also in Ref. 37. In the case of the BMKP potential, which is a full six-dimensional surface31, the transformation from H2-H2 to the H2-HD system was done by shifting the center of mass in one H2 molecule to the center of mass of the HD molecule. Because the DJ PES has been formulated for the rigid monomer rotor model, the transformation methodology was more complicated. Simply, the $\vec{R}_1$ and $\vec{R}_2$ coordinates are not available in this case, they have fixed lengths. In this paper the transformation has been accomplished by rotation of the space fixed OXYZ coordinate system, i.e. by the redirection of the $\vec{R}_3$ vector. The new vector $\vec{R}_3'$ connects the center of masses of the H2 and the HD molecules as shown in the Fig. 2. This procedure obtains new coordinate angles for the Jacobi vectors $\vec{R}_1$, $\vec{R}_2$, and $\vec{R}_3$, and a new PES as in Eq. 20. New experiments that measure the state-to-state rotational cross sections in the HD+α-/p-H2 collisions at low temperatures are needed. Thereafter theoreticians and astrophysicists would be able to compare computational results with available experimental data. This type of work was recently accomplished, for instance, for the para-H2+H2 collision33. Here it would be useful to mention other contributions on hydrogen-hydrogen collisions.48–50 Additionally, with the use of new HD+H2 results for the thermal rate coefficients one could carry out new computation of the HD-cooling function mentioned in the introduction.25 In conclusion, another interesting system worth mentioning is HD+HD. For this collision there are relatively old experimental state-to-state rotational probabilities for a few selected states.51 These old data can be useful in comparisons with the computational results obtained with different H4 PESs: such as the available DJ and the BMKP PESs or some relatively new potentials, for example from works14,52. In the case of the DJ surface it would be possible to again apply the rotation procedure of the OXYZ coordinate system as performed in this paper.

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