Rotational energy transfer in H$_2$+H$_2$

Renat A. Sultanov$^a$ *, Dennis Guster$^a$†.

$^a$Business Computing Research Laboratory, St. Cloud State University, 31 Centennial Hall, 720 Fourth Avenue South, St Cloud, MN 56301-4498

Quantum-mechanical close-coupling calculations for state-to-state cross sections and thermal rates are reported for H$_2$+H$_2$ collisions. Two recently developed potential energy surfaces (PES) for the H$_2$−H$_2$ system are applied, namely, the global potential surface from the work of A.I. Boothroyd, P.G. Martin, W.J. Keogh, M.J. Peterson, J. Chem. Phys., 116 (2002) 666, and a restricted, model surface from the works of P. Diep, J.K. Johnson, J. Chem. Phys., 113 (2000) 3480; ibid. 112, 4465. The low temperature limit is investigated. We found significant differences in cross sections and corresponding thermal rates calculated with these two PESs.

1. Introduction

The investigation of elastic and inelastic collisions between molecules and between molecules and atoms can provide valuable information about interactions, chemical properties and energy transfer dynamics [1-15]. The hydrogen molecule is the simplest and most abundant molecule in the universe’s molecular clouds and plays an important role in many areas of astrophysics. For example, knowledge of the ro-vibrational excitation and de-excitation rate constants in molecular hydrogen collisions is of fundamental importance for understanding and modeling the energy balance in the interstellar medium. The energy transfer processes involving H$_2$ molecules control the evolution of shock fronts and photodissociation regions (PDRs) in the interstellar medium. Additionally, the energy transfer between H$_2$ molecules and between H$_2$ and other atoms/molecules is important for cooling of primordial gas and shock wave-induced heating in the interstellar media. However, to accurately model the thermal balance and kinetics of such important systems one needs accurate state-to-state rate constants $k_{v''j''}(T)$.

Experimental measurement of quantum state resolved cross sections and rates is a very difficult technical problem. On the other hand, accurate theoretical data requires precise potential energy surfaces and reliable dynamical treatment of the collision processes. The first attempt to construct a realistic full-dimensional ab initio PES for the H$_2$−H$_2$ system was done in works [3], and the potential was widely used in a variety of methods and computation techniques.

Recently the H$_2$−H$_2$ system has been re-investigated and an accurate interaction potential from the first principles has been developed in work [12]. However, in this work the Diep and Johnson potential energy surface (DJ PES) was extrapolated only for the rigid rotor monomer model of H$_2$−H$_2$.

An extensive study of the H$_2$−H$_2$ PES has been recently reported by Boothroyd et al. [13], where the potential energies have been represented at 48180 geometries respectively with a large basis set at the multireference configuration interaction level.

In this work we provide a test of sensitivity for the new PESs for collisions of rotationally excited H$_2$ molecules

$$\text{H}_2(j_1) + \text{H}_2(j_2) \rightarrow \text{H}_2(j'_1) + \text{H}_2(j'_2).$$

(1)

We apply only the new surfaces mentioned above.

The scattering cross sections and their corresponding rate coefficients are calculated using a non reactive quantum-mechanical close-coupling approach. In the next section we will briefly outline the method. Our results and discussion are presented in Section 3.

---

$sultanov@bcrl.stcloudstate.edu$; $sultanov2@yahoo.com$

$^a^*$

$^a^†$dcguster@stcloudstate.edu
2. Method

In this section we provide a brief outline of the quantum-mechanical close-coupling approach used in our calculations. All relevant details have been developed in works [1]. The hydrogen molecules are treated as linear rigid rotors. The model has been applied in few previous works, see for example [14]. For the considered range of kinetic energies of astrophysical interest the rotor model is considered to be adequate [13]. The kinetic energy is \( \epsilon \equiv E - B_1j_1(j_1 + 1) - B_2j_2(j_2 + 1) \). Here \( E \) is the total energy in the system, \( B_{1(2)} = 60.8 \, \text{cm}^{-1} \) are the rotation constants of the colliding \( \text{H}_2 \) molecules, \( J \) is total angular momenta of the 4-atomic system, \( \alpha \equiv (j_1j_2j_1L) \), where \( j_1 + j_2 = j_2 \) and \( j_1 + L = J \), \( k_{\alpha\alpha'} = 2M_{12}(E + E_\alpha - E_{\alpha'})^{1/2} \) is the channel wavenumber and \( E_{\alpha} \) are rotational energies.

The log-derivative matrix is propagated to large \( R \)-intermolecular distances, since all experimentally observable quantum information about the collision is contained in the asymptotic behaviour of functions \( U_{\alpha}^{JM}(R \to \infty) \). A set of coupled second order differential equations for the unknown radial functions \( U_{\alpha}^{JM}(R) \) is solved

\[
\frac{d^2}{dR^2} - \frac{L(L+1)}{R^2} + k_{\alpha}^2 U_{\alpha}^{JM}(R) = 2M_{12} \sum_{\alpha'} \int < \phi_{\alpha'}^{JM}(\tilde{r}_1, \tilde{r}_2, \tilde{R}) | V(\tilde{r}_1, \tilde{r}_2, \tilde{R}) | \phi_{\alpha'}^{JM}(\tilde{r}_1, \tilde{r}_2, \tilde{R}) > U_{\alpha'}^{JM}(R) d\tilde{r}_1 d\tilde{r}_2 d\tilde{R},
\]

where \( \alpha \equiv (j_1j_2j_1L) \). We apply the hybrid modified log-derivative-Airy propagator in the general purpose scattering program MOLSCAT [15] to solve the coupled radial equations [3]. Different propagator schemes included in MOLSCAT have been tested. Our calculations showed that other propagators can also provide quite stable results.

The numerical results are matched to the known asymptotic solution to derive the physical scattering \( S \)-matrix

\[
U_{\alpha}(R \to \infty) \approx \delta_{\alpha\alpha'} e^{-i(k_{\alpha\alpha}R - (l\pi/2))} - \left( \frac{k_{\alpha\alpha}}{k_{\alpha\alpha'}} \right)^{1/2} S_{\alpha\alpha'}^J e^{-i(k_{\alpha\alpha}R - (l'\pi/2))},
\]

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, \( R_{\text{max}} \), for all channels included in our calculations.

The relationship between the rate coefficient \( k_{j_1j_2\to j'_1j'_2}(T) \) and the corresponding cross section \( \sigma_{j_1j_2\to j'_1j'_2}(E_{\text{kin}}) \) can be obtained through the following weighted average

\[
k_{j_1j_2\to j'_1j'_2}(T) = \frac{8k_BT}{\pi \mu} \frac{1}{(k_BT)^2} \int_{c_2}^{c_1} \epsilon d\epsilon \sigma_{j_1j_2\to j'_1j'_2}(\epsilon) e^{-\epsilon/k_BT},
\]

where \( \epsilon = E - E_{j_1} - E_{j_2} \) is precollisional translational energy at the translational temperature \( T \), \( k_B \) is Boltzman constant, \( \mu \) is reduced mass of the molecule-molecule system and \( \epsilon_s \) is the minimum kinetic energy for the levels \( j_1 \) and \( j_2 \) to become accessible.

3. Results

As we mentioned in the Introduction, in this work we apply the new PESs from works [12] and [13]. The DJ PES [12] is constructed for the vibrationally averaged rigid monomer model of the \( \text{H}_2-\text{H}_2 \) system to the complete basis set limit using coupled-cluster theory with single, double and triple excitations. A four term spherical harmonics expansion model was chosen to fit the surface. It was demonstrated, that the calculated PES can reproduce the quadrupole moment to within 0.58 % and the experimental well depth to within 1 %.
The bond length was fixed at 1.449 a.u. or 0.7668 Å. DJ PES is defined by the center-of-mass intermolecular distance, $R$, and three angles: $\theta_1$ and $\theta_2$ are the plane angles and $\phi_{12}$ is the relative torsional angle. The angular increment for each of the three angles defining the relative orientation of the dimers was chosen to be 30°.

The BMKP PES [13] 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 as possible van der Waals well. In the six-dimensional conformation space of the four atomic system the conical intersection forms a complicated three-dimensional hypersurface. Because the BMKP PES uses cartesian coordinates to compute distances between four atoms, we have devised some fortran code, which converts spherical coordinates used in Sec. 2 to the corresponding cartesian coordinates and computes the distances between the four atoms. In all our calculations with this potential the bond length was fixed at 1.449 a.u. or 0.7668 Å as in the DJ PES.

A large number of test calculations have also been done to secure the convergence of the results with respect to all parameters that enter into the propagation of the Schrödinger equation [11]. This includes the intermolecular distance $R$, the total angular momentum $J$ of the four atomic system, $N_{tot}$ the number of rotational levels to be included in the close coupling expansion and others (see the MOLSCAT manual [15]). We reached convergence for the integral cross sections, $\sigma(E_{kin})$, in all considered collisions. In the case of the DJ PES the propagation has been done from 2 Å to 10 Å, since this potential is defined only for those specific distances. For the BMKP PES we used $r_{min} = 1$ Å to $r_{max} = 30$ Å. We also applied a few different propagators included in the MOLSCAT program.

Now we present our results for different rotational transitions in collisions between $para/para$- and ortho-/ortho-hydrogen molecules [11]. Our main goal in this work is first: to carry out complete quantum-mechanical calculations with new potentials for different transitions in $p\text{-}H_2+p\text{-}H_2$ and $o\text{-}H_2+o\text{-}H_2$ collisions and, second, to provide a comparative study and check the sensitivity of the two newest surfaces for the very important and fundamental $H_2\text{-}H_2$ system.

The energy dependence of the elastic integral cross sections on the total energy $\sigma_{el}(E_{tot})$ in the $H_2+H_2$ system is represented in Fig. 1 (upper plots) together with the state-resolved integral cross sections $\sigma_{j_1j_2\rightarrow j_1^\prime j_2^\prime}(E_{tot})$ for the $j_1 = j_2 = 0 \rightarrow j_1^\prime = 2, j_2^\prime = 2$ and $j_1 = j_2 = 1 \rightarrow j_1^\prime = 1, j_2^\prime = 3$ rotational transitions (lower plots) for both the BMKP and the DJ PESs respectively. As can be seen both PESs provide the same type of the behaviour in the cross section. These cross sections are in basic agreement with recent time-dependent quantum-mechanical calculations in work [17]. However, our results show, that the DJ PES generates about 30 % higher values for the cross sections relatively to the BMKP PES.

Also, it is important to point out here, that for...
comparison purposes we don’t include the compensating factor of 2 mentioned in [2]. However, in Fig. 2 (left plot) and in our subsequent calculations of the thermal rate coefficients, \( k_{jj'}(T) \), the factor is included.

Significant differences in the cross sections of the two potentials are reflected in the state-resolved transition states \( j_1 = 0, j_2 = 0 \rightarrow j'_1 = 2, j'_2 = 0 \), as shown in Fig. 2 (right panel). That is why it seems that the DJ PES can provide much better results, as seen in the same figure in the left panel. Specifically, when we present the results for the corresponding thermal rates \( k_{00-20}(T) \) calculated with the DJ potential together with results of other theoretical calculations [4] and [5] the agreement is almost perfect. Next, Fig. 3 provides the same results for the cross sections, but includes the details at low energies, together with the corresponding experimental data from [9]. Now one can better see the considerable differences in these two cross sections. However, the DJ PES is able to provide very good agreement with experimental data [9]. Thus we conclude, that DJ PES is much better suited for the \( \text{H}_2-\text{H}_2 \) system. Moreover, in Fig. 4 we provide thermal rates for different transition states calculated with only the DJ PES and in comparison with other theoretical data obtained within different dynamical methods and PESs. Again the agreement is very good.

Finally, Table 1 depicts the thermal rates \( k_{00-20}(T) \) and \( k_{02-32}(T) \) at lower kinetic temperatures, up to 10 K. Numbers in each column should be multiplied by corresponding prefactor \( P \). As can be seen our results are in very good agreement with recent experimental and theoretical data at higher temperatures. However, at \( T < 30 \) K we could not reproduce effectively the results of [9]. It may be because of the interatomic (\( \text{H}_2-\text{H}_2 \)) distance restrictions in the DJ surface in which the potential ranges from 2 Å to only 10 Å. It seems plausible, that for such low energies one needs to carry out calculations even beyond the 10 Å limit.

We provide close-coupling quantum-mechanical calculations of the state-resolved rotational excitation and deexcitation cross sections and rates for molecular hydrogen collisions.

![Figure 2. Temperature dependence of the state-resolved thermal rate constant (left panel) and corresponding cross sections (right panel) for the transition \( j_1 = j_2 = 0 \rightarrow j'_1 = 2, j'_2 = 0 \). Squares and circles are the data from [4] and [5] respectively. Our results with the DJ PES are depicted with solid lines, the open triangles up represent our results with the BMKP surface.](image)

![Figure 3. Cross sections for the 00\rightarrow20 rotational transition calculated with the DJ and BMKP PESs for the \( \text{H}_2+\text{H}_2 \) collision. The circles are some experimental data from the work [9]. triangles up and triangles down are the results of this work using the DJ and BMKP PESs respectively.](image)
Rotational energy transfer

A test of convergence and the results for cross sections and rate coefficients using two different potential energy surfaces for the $\text{H}_2−\text{H}_2$ system have been obtained for a wide range of kinetic energies [11].

Our calculations revealed, that both PESs can provide the same type of behaviour in regard to cross sections and rates for different transition states. However, significant differences in the cross section of the $00\rightarrow 20$ transition have been found. Also, it was already indicated, that at even larger kinetic energies the DJ potential overestimates relative to the BMKP surface the cross sections and rates by about 20–40\% [11].

In conclusion, the results of these calculations show, that additional work is needed to further improve the BMKP PES, particularly the part of the surface, which is responsible for the $00\rightarrow 20$ transition. We also found, as can be verified from Table 1, it is difficult to use the DJ surface and carry out reliable calculations at temperatures lower than 30 K.

Table 1
Thermal rates $k_{00\rightarrow 20}(T)$ and $k_{02\rightarrow 22}(T)$ (m³s⁻¹) at low and very low temperatures calculated with the DJ surface in comparison with available experimental*\) and theoretical data from [9].

| $T$ (K) | DJ  | [4] | [9] | DJ  | [9] | $P$ |
|--------|-----|-----|-----|-----|-----|-----|
| 100    | 1.64| 2.2(4)| 1.92| 2.63| 3.23| $10^{-20}$|
| 60     | 3.81| 6.0(7)| 4.75| 5.62| 7.97| $10^{-22}$|
| 30     | 0.54| 1.1(1)| 0.80| 0.65| 1.34| $10^{-25}$|
| 20     | 0.87| 2.3(3)| 1.63| 0.93| 2.71| $10^{-29}$|
| 10     | 0.38| 2.7(7)| 1.65| 0.33| 2.62| $10^{-40}$|

REFERENCES
1. S. Green, J. Chem. Phys., 62 (1975) 2271.
2. G. Danby, D.R. Flower, T.S. Monteiro, Mon. Not. R. Astr. Soc., 226 (1987) 739.
3. D.W. Schwenke, J. Chem. Phys., 89 (1988) 2076; 1990, J. Chem. Phys., 92, 7267
4. D.R. Flower, Mon. Not. R. Astron. Soc., 297 (1998) 334.

Figure 4. Thermal rates calculated with the DJ PES for the $00 \rightarrow 22$, $02 \rightarrow 22$, $20 \rightarrow 00$ and $11 \rightarrow 13$ transitions and other results [24].

5. D.R. Flower, E. Roueff, J. Phys. B: At. Mol. Opt. Phys., 31 (1998) 2935.
6. S.K. Pogrebnya, D.C. Clary, Chem. Phys. Lett., 363 (2002) 523.
7. S.Y. Lin, H. Guo, Chem. Phys. 289 (2003) 191.
8. M. Bartolomei, M.I. Hernandez, J. Campos-Martinez, J. Chem. Phys., 122 (2005) 064305.
9. B. Mate, F. Thibault, G. Tejeda, J.M. Fernandez, S. Montero, J. Chem. Phys., 122 (2005) 064313.
10. F. Gatti, F. Otto, S. Sukiasyan, H.-D. Meyer, J. Chem. Phys. 123 (2005) 174311.
11. R.A. Sultanov, D. Guster, Chemical Physics, in press 2006.
12. P. Diep, J.K. Johnson, J. Chem. Phys., 113 (2000) 3480; ibid. 112 (2000) 4465.
13. A.I. Boothroyd, P.G. Martin, W.J. Keogh, M.J. Peterson, J. Chem. Phys., 116 (2002) 666.
14. J. Le Bourlot, G. Pineau des Forets, D.R. Flower, Mon. Not. R. Astron. Soc., 305 (1999) 802.
15. J.M. Hutson, S. Green, MOLSCAT VER. 14 (1994) (Distributed by Collabor. Comp. Proj. 6, Daresbury Lab., UK, Eng. Phys. Sci. Res. Council, 1994)