

Rotational Quenching of HD in Collisions with H₂: Resolving Discrepancies for Low-lying Rotational Transitions

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Abstract

The deuterated hydrogen molecule HD has been observed in a variety of cool molecular astrophysical environments. By virtue of its small dipole moment the HD molecule is believed to have played an important role in the cooling of the primordial gas in the formation of the first stars and galaxies. HD has also recently been proposed as a tracer of molecular hydrogen in protoplanetary disk evolution, providing a diagnostic for the total disk mass. Here we report benchmark computations of rotational quenching rate coefficients for HD in collisions with H₂ based on quantum coupled channel methods within the rigid rotor model, and validate them against full-dimensional rovibrational scattering formalism. It is found that the rigid rotor model yields accurate rate coefficients for rotational transitions in HD+H₂ collisions at astrophysically relevant kinetic temperatures. Results are reported using the most recent highly accurate interaction potentials for the H₂-H₂ system. We obtain excellent agreement with previous results of Schaefer for the most important $\Delta j = \pm 1$, ± 2 transitions in HD induced by ortho- and para-H₂, but find significant differences with recent results of Sultanov et al. that employed the same interaction potential as the one adopted here.

Key words: early universe – ISM: molecules – molecular data – molecular processes – photon-dominated region (PDR) – protoplanetary disks

1. Introduction

Protoplanetary disks around young stars are the sites of planet formation. Their evolution and dispersal determine the environments in which planets are born (Armitage 2011). A fundamental property of protoplanetary disks is their total mass which is difficult to quantify (McClure et al. 2016). In the field of planet formation, the disk gas mass at various stages of evolution forms the initial conditions in planetary population synthesis models (Mordasini et al. 2012). The main component of the gas in protoplanetary disks is H₂, which is difficult to detect as it has no dipole moment. For this reason, two proxies are generally used as tracers for H₂: sub-millimeter observations of thermal emission from dust grains and emission lines from carbon monoxide (Bergin et al. 2013; McClure et al. 2016; Trapman et al. 2017). However, conversion from dust emission to gas mass requires knowledge of grain properties, dust/gas mass ratio, dust opacities etc., which are uncertain and may differ from interstellar values. On the other hand, CO emission lines generally only provide information about the disk surface as the CO/H_2 ratio may vary with disk height and distance from the star due to UV photodissociation in the surface layers and freeze-out of CO in the cold midplane (Dutrey et al. 1997; van Zadelhoff et al. 2001; Reboussin et al. 2015; McClure et al. 2016). As a result, mass estimates of protoplaneray disks vary by orders of magnitude, as in the case of TW Hydrae for which the predicted range is 0.0005-0.06 solar masses (Weintraub et al. 1989; Calvet et al. 2002; Thi et al. 2010; Bergin et al. 2013).

Bergin et al. (2013) recently suggested the use of HD as a tracer of disk gas because it closely follows the distribution of molecular hydrogen and its emission is sensitive to the total disk mass. Using the *Herschel Space Observatory* Photodetector Array Camera Spectrometer they robustly (9σ)

detected the fundamental $j = 1 \rightarrow 0$ rotational transition of HD at ~112 μ m from the direction of TW Hya. The $j = 1 \rightarrow 0$ emission line of HD has also been previously detected by the *Infrared Space Observatory* Long Wavelength Spectrometer in the direction of the Orion Bar (Wright et al. 1999; Bergin et al. 2013). Other transitions in HD have also been detected in shock-heated gas and supernovae outflows from massive stars (Bertoldi et al. 1999; Neufeld et al. 2006; Bergin et al. 2013). The rotational population of HD is sensitive to the gas temperature, and its collisional excitation by ambient gas, primarily H₂, needs to be accurately determined as a function of the temperature. Collisions with both ortho- and para-H₂ are needed as the ortho–para ratio of H₂ may differ significantly in different astrophysical environments.

Apart from its importance in disk gas modeling, HD is thought to play an important role in the cooling of the primordial gas and early universe chemistry models. It has long been acknowledged that H₂ is the main coolant in the primordial gas during the formation of the first baryonic objects. However, due to its lack of a permanent dipole moment, only quadrupole transitions are possible for H₂, leading to $\Delta i = \pm 2$ transitions. By virtue of its smaller rotational constant and permanent (though weak) electric dipole moment, cooling by HD cannot be neglected (Galli & Palla 2013). Although the HD/H_2 abundance ratio after freeze-out is about 10^{-3} (Puy et al. 1993; Galli & Palla 1998; Stancil et al. 1998; Flower 2000, 2007), HD may contribute significantly relative to H₂ in cooling the astrophysical media. Collisional excitations/de-excitations of HD with He, H, and H₂ have previously been reported by a number of authors (Schaefer 1990; Flower 1999, 2000; Flower & Roueff 1999a, 1999b; Roueff & Flower 1999; Roueff & Zeippen 1999, 2000; Flower et al. 2000; Nolte et al. 2012). The smaller spacing between energy levels of HD and its larger collisional rate

coefficients allow for enhanced excited-state populations and greater rates of energy transfer between the radiation field and matter (Flower 2000; Coppola et al. 2011; Nolte et al. 2012).

In a series of papers, Sultanov et al. (2009, 2012, 2016) have reported extensive calculations of rotational transitions in HD+H₂ collisions using a rigid rotor model and the H₂-H₂ potential energy surfaces (PESs) of Boothroyd et al. (1991), referred to as the BMKP PES, a four-dimensional rigid rotor PES by Diep & Johnson (2000a, 2000b), referred to as the DJ potential, as well as a rigid rotor version of a six-dimensional PES by Hinde (2008). While their initial studies (Sultanov et al. 2009) using the BMKP PES yielded results in reasonable agreement with earlier results of Schaefer (1990) as well as Flower (1999) and Flower & Roueff (1999a), their more recent results on the DJ (Sultanov et al. 2012) and the Hinde PESs (Sultanov et al. 2016) appear to be very different. Indeed, their latest studies (Sultanov et al. 2016) on the Hinde PES yielded results that are qualitatively and quantitatively different from those reported by Schaefer (1990) and their own previous results (Sultanov et al. 2009) on the BMKP PES. However, no explanation was given for the source of the discrepancy. This has created considerable confusion and uncertainty surrounding available rate coefficients for rotational transitions in the HD+H₂ system. Further, this calls into question the validity of Schaefer's results, which are generally considered to be accurate for rotational transitions in HD+H2 collisions (Flower 1999; Flower & Roueff 1999a).

The purpose of this paper is to report both full-dimensional and four-dimensional quantum close-coupling calculations of rotational transitions in HD+H₂ collisions using the two most recent and accurate PESs for the H₂–H₂ system by Hinde (2008) and Patkowski et al. (2008) and compare them against the previous studies of Schaefer (1990) and the recent results of Sultanov et al. (2012, 2016). It is found that both PESs yield similar results and reproduce Schaefer's results quantitatively for most low-lying rotational transitions. In particular, the Hinde PES yields results in almost complete agreement with that of Schaefer for the dominant rotational transitions in HD. The Hinde and Patkowski PESs yield similar results except at collision energies well below 1 K but these differences do not manifest in rate coefficients above 5 K of interest in astrophysical media.

The paper is organized as follows: In Section 2 a brief description of available PESs of the H_2 - H_2 system is provided, the computational details are given in Section 3, results are presented in Section 4, and a summary of our findings is given in Section 5.

2. PESs for the H₂-H₂ System

Being the lightest neutral four-atom system, there is a long history of development of interaction potentials for the H₂–H₂ system. Within the Born–Oppenheimer approximation, the PESs for the ground states of H₂–H₂ and H₂–HD are the same except that the center of mass of HD is slightly shifted from that of H₂. A detailed discussion on the early developments of H₂–H₂ PESs is given by Schaefer (1990). The first attempt to compute rate coefficients for rotational transitions in HD+H₂ collisions was by Chu. (1975) who used an empirically determined isotropic potential for H₂–H₂. Subsequently, Schaefer (1990) carried out detailed quantum close-coupling calculations for HD+H₂ collisions involving both ortho- and para-H₂ using a semi-empirical PES and provided tabulated values of rate coefficients for transitions among j = 0-2 for HD and j = 0-3 for H₂ for temperatures ranging from 10 to 300 K. This was followed by calculations of Flower (1999) and Flower & Roueff (1999a) who used the ab initio PES developed by Schwenke (1988), which also allows treatment of vibrational transitions. The computations of Flower and co-workers (Flower 1999; Flower & Roueff 1999a) yielded comparable results to those of Schaefer (1990) for the dominant $\Delta j = \pm 1$ transitions in HD but significant differences (an order of magnitude or larger) were seen for transitions that involve exchange of two rotational quanta between the two molecules such as HD(j = 2)+H₂(j = 0) \rightarrow HD(j = 0)+H₂(j = 2) or vice versa. This is most likely due to the uncertainties in the higher-order angular anisotropic terms of the interaction potentials employed in these calculations.

Subsequent to these calculations, several newer and more accurate ab initio electronic PESs have been reported for the H₂-H₂ system (Diep & Johnson 2000a, 2000b; Hinde 2008; Patkowski et al. 2008). These include the four-dimensional rigid rotor PESs by Diep & Johnson (2000a, 2000b) as well as by Patkowski et al. (2008), and the six-dimensional PES by Hinde (2008). The potential surfaces of Hinde (2008) and Boothroyd et al. (1991) are the only full-dimensional PESs available for the H₂-H₂ system. We have previously reported extensive computations of H2+H2 collisions on the BMKP (Quéméner et al. 2008; Quéméner & Balakrishnan 2009), DJ (Lee et al. 2008), and Hinde (Balakrishnan et al. 2011; Fonseca dos Santos et al. 2013) PESs. However, due to the inaccuracy in the treatment of the long-range interaction, rate coefficients computed on the BMKP PES were found to be less accurate than that obtained using the DJ and Hinde PESs. The PESs of Hinde and Patkowski et al. provide an accurate treatment of the long-range interaction and are the most accurate ab initio interaction potentials for the H2-H2 system. The surface of Patkowski et al. employs a higher level of electronic structure theory and its analytic fit includes higher-order anisotropic terms than that of the Hinde PES but it is restricted to the rigid rotor geometry. For this reason, we have adopted the Hinde PES in our previous studies of rovibrational transitions in H₂+H₂ collisions. The PES of Patkowski et al. has recently been adopted in large-scale computations of rotational transitions in H_2+H_2 collisions (Wan et al. 2018). However, it has so far not been adopted in HD+H₂ collisions. A six-dimensional hybrid PES for the H₂+H₂ system that combines the PES of Patkowski et al. for rigid rotor geometries and the Hinde PES for non-rigid rotor geometries has also been developed (Garberoglio et al. 2012). Our exploratory calculations on this potential have yielded results similar to that on the Hinde PES for both rotational and vibrational transitions in H_2+H_2 collisions.

3. Computational Details

Computations are performed using the quantum closecoupling method of Arthurs & Dalgarno (1960). Details are given in our prior publications on the H_2 – H_2 system (Quéméner et al. 2008; Quéméner & Balakrishnan 2009; Balakrishnan et al. 2011) as well as Schaefer (1990) and Flower (1999). The main difference here, compared to H_2 + H_2 collisions, is that for the HD– H_2 system, the center of mass of the HD molecule is shifted from that of H_2 and the potential energy surface needs to be expressed in this new coordinate system. In our work this is accomplished by a coordinate rotation similar to that described by Sultanov et al. (2012, 2016) in which the center-of-mass vector (\mathbf{R}) connecting the centers of mass of the two H₂ molecules is rotated to coincide with that of the HD molecule. However, we found some mistakes in the formulas given in Sultanov et al. (2012) (e.g., in the line above Equation (23) $\sin(\pi - \theta_2)$ was incorrectly given as $\cos \theta_2$ which affected Equations (23) and (24) and led to a wrong expression for the rotation angle given by Equation (21)). The wrong rotation angle would yield an incorrect potential and unphysical cross sections. However, we do not know if these expressions were actually used in the calculations of Sultanov et al.. Such a rotation was not required for the BMKP PES (Boothroyd et al. 1991) because it is given in terms of internuclear distances. Corrected formulas for the coordinate rotation following the same approach as that of Sultanov et al. are provided in the Appendix.

The angular dependence of the interaction potential is expanded as (Quéméner & Balakrishnan 2009)

$$U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) = \sum_{\lambda} A_{\lambda}(r_1, r_2, \mathbf{R}) Y_{\lambda}(\hat{r}_1, \hat{r}_2, \hat{\mathbf{R}}), \qquad (1)$$

with

$$Y_{\lambda}(\hat{r}_{1}, \hat{r}_{2}, \hat{R}) = \sum_{m} \langle \lambda_{1} m_{1} \lambda_{2} m_{2} | \lambda_{12} m_{12} \rangle \\ \times Y_{\lambda_{1} m_{1}}(\hat{r}_{1}) Y_{\lambda_{2} m_{2}}(\hat{r}_{2}) Y^{*}_{\lambda_{12} m_{12}}(\hat{R}),$$
(2)

where $\lambda \equiv \lambda_1 \lambda_2 \lambda_{12}$, $m \equiv m_1 m_2 m_{12}$, and $\langle \lambda_1 m_1 \lambda_2 m_2 | \lambda_{12} m_{12} \rangle$ is a Clebsch–Gordan coefficient.

The total nuclear wave function is expanded in a basis set of rovibrational eigenfunctions of the two molecules. For collisions between two distinguishable molecules (like $HD+H_2$), the above expansion of the interaction potential in the Schrödinger equation yields the following set of coupled equations (Quéméner & Balakrishnan 2009):

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2 l(l+1)}{2\mu R^2} + \varepsilon_{vj} - E \right\} F_{vjl}^{JM}(R) + \sum_{\lambda \nu' j' l'} \mathcal{U}_{vjl,\nu' j' l'}^{JM;\lambda}(R) F_{\nu' j' l'}^{JM}(R) = 0,$$
(3)

where μ is the reduced mass, $F_{\nu'j'l'}^{JM}(R)$ are the radial expansion coefficients of the wave function, and $\mathcal{U}_{\nu j l, \nu' j' l'}^{JM; \lambda}(R)$ are the matrix elements of the interaction potential between the rovibrational wave functions. The total energy is $E = \varepsilon_{\nu j} + E_c$ where $\varepsilon_{\nu j} = \varepsilon_{\nu_1 j_1} + \varepsilon_{\nu_2 j_2}$ is the rovibrational energy of the two separated molecular fragments and E_c is the collision energy. The quantum numbers J and l denote the total angular momentum and orbital angular momentum of the collision pair. The state-to-state cross section is given by

$$\sigma_{\nu_1 j_1 \nu_2 j_2 \to \nu_1' j_1' \nu_2' j_2'}(E_c) = \frac{\pi}{(2j_1 + 1)(2j_2 + 1)k^2} \\ \times \sum_{j_1 2j_1' 2ll'J} (2J + 1)|\delta_{\nu_1 j_1 \nu_2 j_2, \nu_1' j_1' \nu_2' j_2'} \\ - S_{\nu_1 j_1 \nu_2 j_2, \nu_1' j_1' \nu_2' j_2'}^J(E_c)|^2, \tag{4}$$

where the wave vector $k^2 = 2\mu E_c/\hbar^2$.

We have implemented the above formalism for extensive computations of cross sections and rate coefficients for H_2+H_2 (Quéméner et al. 2008; Quéméner & Balakrishnan 2009;



Figure 1. Cross sections for $v_1 = 0$, $j_1 = 1 \rightarrow v'_1 = 0$, $j'_1 = 0$ transition in HD induced by collisions with para-H₂($v_2 = 0$, $j_2 = 0$). The blue curve corresponds to a rigid rotor model while the red curve is from a full-dimensional calculation. Both results correspond to the Hinde (2008) PES.

Balakrishnan et al. 2011; Fonseca dos Santos et al. 2013) and H_2+CO (Yang et al. 2015, 2016) collisions, including vibrational and rotational transitions involving both molecules. Here, we focus primarily on rotational transitions within the ground vibrational levels of the two molecules adopting a rigid rotor approximation. We will explicitly test the validity of this approximation by comparing results from the rigid rotor model against full-rovibrational calculations.

4. Results

We have employed both TwoBC (Krems 2006) and MOLSCAT (Hutson & Green 1994) to perform the closecoupling calculations. The TwoBC code is used for the fulldimensional calculations and the MOLSCAT code is used for the 4D-rigid rotor calculations. Note that MOLSCAT was also used in the computations of Sultanov et al. (2009, 2012, 2016). For the rigid rotor model we used rotational levels $j_1 = 0-4$ for HD and $j_2 = 0$, 2, and 4 for para-H₂ and $j_2 = 1$, 3, and 5 for ortho-H₂. A larger basis set with $j_1 = 0-6$ yielded nearly identical results. For the Hinde PES, the expansion coefficients λ_1 and λ_2 are restricted to 0, 1, and 2 for HD and 0 and 2 for H₂. For the Patkowski et al. PES, $\lambda_1 = 0$ -4 and $\lambda_2 = 0$, 2, and 4 are included. In the rovibrational calculations using the TwoBC code, only the v = 0 vibrational level is included for both molecules with rotational basis taken to be the same as that of the rigid rotor calculations. We restrict our computations to rotational transitions within the v = 0 vibrational levels of both molecules and omit the vibrational quantum number in the label for the cross sections and rate coefficients. We have also separately investigated pure rotational transitions in HD within the v = 1 vibrational level with an expanded basis set which yielded comparable values as that of v = 0 (not presented here).

First we provide a comparison of cross sections from the rigid rotor model against full-dimensional calculations on the Hinde PES to demonstrate the reliability of the rigid rotor approximation for rotational transitions in HD induced by H₂ when both molecules are in their ground vibrational levels. Figure 1 shows a comparison of cross sections for HD($j_1 = 1$)+H₂($j_2 = 0$) \rightarrow HD($j_1 = 0$)+H₂($j_2 = 0$) collisions obtained using the fulldimensional calculations using the TwoBC code and the rigid



Figure 2. Cross sections for $v_1 = 0$, $j_1 = 1 \rightarrow v'_1 = 0$, $j'_1 = 0$ transition in HD induced by collisions with ortho-H₂($v_2 = 0$, $j_2 = 1$). The blue curve corresponds to rigid rotor calculations while the red curve is from a full-dimensional calculations on the Hinde (2008) PES.

rotor calculations using the MOLSCAT code on the Hinde PES. It is seen that both calculations yield essentially identical results except for the small differences in the magnitude and location of the low-energy resonances. Similar comparisons for $j_1 = 1 \rightarrow 0$ transition in HD induced by ortho- $H_2(j_2 = 1)$ are shown in Figure 2. Cross sections for ortho-H₂ collisions exhibit a few more resonances in the 0.1-1 K range due to the broader range of orbital angular momentum quantum numbers present when H₂ is rotationally excited. Results for $j_1 = 2 \rightarrow 0$ and $j_1 = 2 \rightarrow 1$ rotational transitions in HD by $H_2(j_2 = 0)$ are shown in Figure 3. The agreement is remarkably good for both transitions. Similar comparisons are obtained for ortho- $H_2(j_2 = 1)$ collisions and are not reproduced here. These cross sections, when converted to rate coefficients, agree to within 5% in the temperature range of 10-2000 K. They illustrate that the rigid rotor model is adequate to compute rate coefficients for rotational transitions in $HD(v = 0) + H_2$ collisions. Employing a vibrationally averaged potential may provide even better agreement with fulldimensional results. Faure et al. (2016) found this approach yielded improved agreement with full-dimensional calculations compared to rigid rotor approximation for CO+H₂ collisions. Unless indicated otherwise, the rest of the results presented here are obtained within the rigid rotor formalism with HD and H₂ distances kept at their vibrationally averaged values of 1.442 and 1.449 bohr, respectively.

Figure 4 presents a comparison of cross sections for the $j_1 = 1 \rightarrow 0$ transition in HD induced by $H_2(j_2 = 0)$ as a function of the relative velocity obtained from the PESs of Hinde (2008) and Patkowski et al. (2008) with that of Schaefer (1990). All three results display two prominent resonances at about 30–60 and 300 m s⁻¹ though the position of the low-energy resonance is slightly displaced due to the sensitivity of the results at low energies. The position and width of the resonance at 300 m s⁻¹ (collision energy of ~4.5 cm⁻¹) is almost exactly the same in all three calculations. Indeed, the results are nearly indistinguishable for relative velocities beyond 100 m s⁻¹ (relative collision energy ~0.51 cm⁻¹). This illustrates that the leading anisotropic term (A_{101}) of the HD–H₂ interaction that drives the $\Delta j_1 = \pm 1$ transition in HD is accurately characterized by all three potentials. This anisotropic term along with the A_{022} term that drives the $\Delta j_2 = \pm 2$



Figure 3. Cross sections for $j_1 = 2 \rightarrow j'_1 = 1$, 0 transitions in HD induced by collisions with para-H₂($v_2 = 0$, $j_2 = 0$). Results from the rigid rotor model are compared against full-dimensional calculations on the Hinde (2008) PES.



Figure 4. Cross sections for $j_1 = 1 \rightarrow 0$ transition in HD induced by collisions with para-H₂($j_2 = 0$) as a function of the relative velocity. Results from the Hinde (2008) and Patkowski et al. (2008) PESs within the rigid rotor model are compared against previous results of Schaefer (1990) on an empirically determined PES for HD–H₂.



Figure 5. Leading anisotropic terms, A_{101} and A_{022} (see Equation (1)) of the HD–H₂ interaction potential as a function of the center-of-mass separation for the Hinde (2008) and Patkowski et al. (2008) PESs.



Figure 6. Rate coefficients for $j_1 = 1 \rightarrow 0$ transition in HD induced by collisions with para-H₂($j_2 = 0$) as a function of temperature. Results from the present study on the Hinde (2008; black curve) and Patkowski et al. (2008; green curve) PESs are compared against those of Schaefer (1990; red circles) and Sultanov et al. (2016; blue curve).

transition in H_2 are shown in Figure 5 for the PESs of Hinde (2008) and Patkowski et al. (2008). It is seen that these leading anisotropic terms of the interaction potential are nearly identical for both PESs.

Figure 6 compares rate coefficients for $j_1 = 1 \rightarrow 0$ transition in HD by collisions with $H_2(j_2 = 0)$ as a function of the temperature from the present work on the Hinde and Patkowski PESs with those of Schaefer (1990) and Sultanov et al. (2016). It is seen that the present results are nearly indistinguishable from those of Schaefer while showing significant deviation from those of Sultanov et al. The latter are about a factor of 2 larger. Similar comparisons for $j_1 = 1 \rightarrow 0$ transition due to ortho- $H_2(j_2 = 1)$ collisions are presented in Figure 7. Again, excellent agreement is found with Schaefer's results and not with those of Sultanov et al. We note that large discrepancies were also present in the results of Sultanov et al. (2012) obtained using the DJ PES where a similar coordinate rotation was applied.

Figure 8 provides a comparison of rate coefficients from the present study on the Hinde PES for $HD(j_1 = 2)$ + $H_2(j_2 = 0) \rightarrow HD(j_1') + H_2(j_2')$ collisions with those of Schaefer as a function of the temperature. Results on the PES of Patkowski et al. are very similar and are not shown for clarity. It is seen that the present results agree with those of Schaefer for the $(2, 0) \rightarrow (1, 0)$, $(2, 0) \rightarrow (0, 0)$ and $(2, 0) \rightarrow (1, 2)$ transitions. However, significant differences (about an order of magnitude) are observed for the $(2, 0) \rightarrow (0, 2)$ transition which involves an exchange of two rotational quanta between the two molecules. This indicates that, while the leading-order anisotropic term is accurately accounted for in the two potentials, the higher-order anisotropic terms are perhaps not accurately represented in the interaction potential employed by Schaefer. We emphasize that the Hinde and Patkowski PESs yield very similar results for various transitions between rotational levels $j_1 = 0-2$ of HD and $j_2 = 0-3$ of H₂.

Finally, we would like to draw attention to some very recent measurements of collisional relaxation of vibrationally and rotationally excited HD in the v = 1, j = 2 level by H₂ and D₂ at a temperature of about 1 K. In this experiment (Perreault et al. 2017a, 2017b), HD and H₂/D₂ were co-expanded in a supersonic beam and HD was selectively pumped to the v = 1, j = 2 level through a Stark-induced adiabatic Raman passage



Figure 7. Rate coefficients for $j_1 = 1 \rightarrow 0$ transition in HD induced by collisions with ortho-H₂($j_2 = 1$) as a function of the temperature. Results from the present study on the Hinde (2008; black curve) and Patkowski et al. (2008; green curve) PESs are compared against those of Schaefer (1990; red circles) and Sultanov et al. (2016; blue curve).



Figure 8. Rate coefficients for $HD(j_1 = 2)+H_2(j_2 = 0) \rightarrow HD(j'_1)+H_2(j'_2)$ collisions as a function of the temperature from the present work on the Hinde PES and previous results of Schaefer (1990). The different curves are labeled by the final rotational levels of $HD(j'_1)$ and $H_2(j'_2)$. Lines denote the present results and symbols represent those of Schaefer.

scheme. The rotationally relaxed HD in the v = 1, j = 0, 1 states was subsequently detected using time-of-flight spectroscopy. The experiment measured angular distribution of the scattered HD near a collision energy of 1 K and this distribution was found to be sensitive to the initial orientation of HD with respect to the molecular beam axis which was controlled by selecting its initial m_j state. The differential cross sections computed using the Hinde PES (Croft et al. 2018) were found to quantitatively account for the key features of the experiments, providing a sensitive and independent test for the accuracy of the PESs employed in the present calculations.

5. Summary

We have presented explicit close-coupling calculations of rotational transitions in HD induced by ortho- and para-H₂. Two recent and most accurate interaction potentials for the H_2-H_2 system are employed in the scattering calculations: the six-dimensional potential energy surface of Hinde (2008) and the four-dimensional rigid rotor potential of Patkowski et al. (2008). It has been demonstrated that the four-dimensional

rigid rotor model is adequate to compute rotational transitions within the v = 0 vibrational level of HD. It is also found that the interaction potentials of Hinde and Patkowski et al. yield nearly identical results for rotational transitions in HD+H₂ collisions for energies above 1 cm^{-1} . Results from these two potentials are found to be in excellent agreement with those of Schaefer except for transitions involving the exchange of two rotational quanta between the two molecules. On the other hand, our computed results are found to be significantly different from those presented by Sultanov et al. for all rotational transitions in HD+H₂ collisions reported in their work. Because the present calculations and those of Sultanov et al. employed the same Hinde PES and MOLSCAT scattering code, we conclude that the discrepancies raised in the paper of Sultanov et al. were due to a numerical error such as the incorrect rotation angle described in Section 3.

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Appendix

Here we give expressions for the coordinate rotation that shifts the center of mass of HD to H₂. We use the same procedure, coordinate system, and notation as in Sultanov et al. (2012). For details we refer to the coordinate system depicted in Figure 2 of Sultanov et al. (2012) and associated discussions. The Jacobi vectors \mathbf{R}_1 and \mathbf{R}_2 denote the distance vectors of H₂ (formed by atoms 1 and 2) and HD (formed by atoms 3 and 4 with the D atom labeled as 3), and R'_3 denotes the vector connecting the center of mass of H₂ to HD, the latter designated by $O_{\rm HD}$ (note that in the main text we have used r_1 and r_2 for HD and H_2 distance vectors and **R** for the vector connecting the centers of mass of the two molecule,s but this should not cause any confusion). The origin of the space-fixed coordinate system (OXYZ) is located at the center of mass of H₂, i.e., at the center of R_1 . Rotation of this coordinate system by an angle η causes \mathbf{R}'_3 to coincide with \mathbf{R}_3 , the center of mass of H₂ (i.e., if HD were H₂), denoted by O_{H2} . We assume R_2 , R'_3 and R_3 remain in the same *XOZ* plane. We denote the Jacobi coordinates appropriate for H₂+HD scattering as R_1 , R_2 , R'_3 , θ'_1 , θ'_2 and ϕ'_{12} where θ'_1 is the Jacobi angle between R_1 and R'_3 , θ'_2 is the Jacobi angle between \mathbf{R}_2 and \mathbf{R}'_3 and ϕ'_{12} is the out-of-plane twist angle. The coordinate system appropriate for H_2+H_2 is $R_1, R_2, R_3, \theta_1, \theta_2$ and ϕ_{12} . The lengths of the vectors R_1 and R_2 are invariant to the rotation and we will omit them in further discussions. The rotation shifts the center of mass of HD to H₂

shift is given by
$$\mathbf{x} = \mathbf{R}_2 \left(\frac{m_{\rm D}}{m_{\rm D} + m_{\rm H}} - \frac{1}{2}\right) \approx \mathbf{R}_2/6$$

where $m_{\rm H}$ and $m_{\rm D}$ are the masses of the H and D atoms. Our task is to find expressions for R_3 , η , θ_1 , θ_2 and ϕ_{12} in terms of the primed quantities. R_3 is given by

and this

$$R_3 = \sqrt{R_3'^2 + x^2 - 2R_3' x \cos \theta_2'}.$$
 (5)

From the triangle $\Delta O_{\text{HD}}O_{\text{H}_2}O$ (Sultanov et al. 2012), we have $\eta + \theta'_2 + \pi - \theta_2 = \pi$ or $\theta_2 = \theta'_2 + \eta$. Applying the law of sines for this triangle yields

$$\frac{x}{\sin \eta} = \frac{R_3}{\sin \theta_2'} = \frac{R_3'}{\sin(\pi - \theta_2)} = \frac{R_3'}{\sin \theta_2} = \frac{R_3'}{\sin(\theta_2' + \eta)}$$
(6)

which yields

$$\cot \eta = \frac{R_3' - x \cos \theta_2'}{x \sin \theta_2'} \tag{7}$$

which differs from Equation (21) of Sultanov et al. (2012). Finally, the angles θ_1 and ϕ_{12} are given by (Varshalovich et al. 1988) (see ch. 1–4, pp 21–23):

$$\cos\theta_1 = \cos\theta_1' \cos\eta - \sin\theta_1' \sin\eta \cos\phi_{12}' \tag{8}$$

$$\cot \phi_{12} = \cot \phi_{12}' \cos \eta + \frac{\cot \theta_1' \sin \eta}{\sin \phi_{12}'}.$$
 (9)

In the computations, we choose Jacobi coordinates R'_3 , θ'_1 , θ'_2 , and ϕ'_{12} appropriate for the H₂+HD system but rotate the coordinate system to R_3 , θ_1 , θ_2 , and ϕ_{12} to evaluate the H₂-H₂ interaction potential which is expressed in this coordinate system.

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