

## REGULAR ARTICLE

# An Investigation of Electronic Nonadiabaticity in the D + HBr and H + DBr Reaction on New Diabatic Potential Energy Surfaces

Ai-Jie Zhang\*, Jian-Feng Jia and Hai-Shun Wu

\*School of Chemistry and Material Science, Shanxi Normal University, Linfen China, P. R. 041004

Received 18 December 2012; Accepted (in revised version) 19 January 2013

*Special Issue: Guo-Zhong He Festschrift*

---

**Abstract:** Time-dependent wave packet calculations were carried out to investigate possible electronic nonadiabaticity in the D + HBr and H + DBr reactions on the new fitted diabatic potential energy surfaces by Han and coworkers [J. Chem. Phys., 137 (2012), 194305]. Reaction probabilities and integral cross sections are calculated. The results show negligible nonadiabatic effect for the title reactions in the energy range considered here, which is in accordance with the H + HBr and D + DBr reactions.

**AMS subject classifications:** 70F07, 74J20

**Key words:** Potential energy surfaces, Time-dependent wave packet, Nonadiabatic effect

---

## 1 Introduction

The reactions of H + HBr [1-6] and Br + H<sub>2</sub> [7-10] are of fundamental importance in the development and understanding of elementary chemical kinetics and reaction dynamics, and play key roles in the hydrogen-bromine flame system [11]. The previous experimental investigations have been largely focused on the determination of reaction rates of the H + HBr abstraction and H + H'Br exchange reactions and kinetic isotope effects. However, due to the large mass of the Br atom and the very low barrier height of the H + HBr abstraction reaction (about 1.6 kcal/mol), it is a great challenge to accurately simulate multiple coupled

---

\* Corresponding author. *Email address:* zaj@dicp.ac.cn (Ai-Jie Zhang)

potential energy surfaces for the BrH<sub>2</sub> system.

The approach of molecular hydrogen to an atom Br in a <sup>2</sup>P electronic state splits the degeneracy of this state, giving rise to three PESs [16]. Among them, two electronic states (<sup>1</sup>2 A' and <sup>1</sup>2 A'' ; <sup>2</sup>Σ<sup>+</sup> and <sup>2</sup>Π in linear geometry) correlate adiabatically with the ground-state atomic reactant Br(<sup>2</sup>P<sub>3/2</sub>) while a third state (<sup>2</sup>2 A'; <sup>2</sup>Π in linear geometry) correlates adiabatically with the excited-state atomic reactant Br(<sup>2</sup>P<sub>1/2</sub>) which is denoted by Br\*. Of these, only the <sup>1</sup>2 A' electronic state correlates with the electronic ground state of the products (HBr(X<sup>1</sup>Σ<sup>+</sup>) + H (<sup>2</sup>S)). The PESs of the other states (<sup>1</sup>2 A'' and <sup>2</sup>2 A' ) correlate with HBr products in the a<sup>3</sup>Π electronic state, which is considerably higher in energy [16]. Thus, if the Br + H<sub>2</sub> reaction were to proceed adiabatically on a single PES, as would be predicted by the Born-Oppenheimer (BO) approximation, then the excited SO state would not react. Based on the microscopic reversibility idea, the reaction H + HBr → Br\* + H<sub>2</sub> (and other isotopic variants) would not occur at the presence of BO approximation. The excited Br\* atom will be obtained mainly by means of nonadiabatic transition from ground PES to the excited PES via spin-orbit coupling element [14].

In the experimental aspects, inelastic and reactive scattering of Br\*(<sup>2</sup>P<sub>1/2</sub>) with H<sub>2</sub> have been investigated by Nesbitt and Leone [12] by a systematic laser photolysis. They concluded that Br\* + H<sub>2</sub> (v = 1) is efficiently quenched to Br + H<sub>2</sub> (v = 2) in the entrance channel, followed by subsequent H atom abstraction from vibrationally excited H<sub>2</sub>. In 2005, Zare and co-workers [6] measured the rotational state distribution for the H + HBr → H<sub>2</sub> (v' = 2, j') + Br reaction at 53 kcal/mol collision energy and observed a small fraction of the H<sub>2</sub> molecule produced in highly rotationally excited states. Based on quasi-classical trajectory (QCT) calculations on a London-Eyring-Polanyi-Sato (LEPS) potential energy surface, they presented two distinct mechanisms: a direct reactive mechanism in which the trajectories stay near the collinear minimum energy path, and an indirect reactive mechanism in which the trajectories deviate significantly from the minimum energy path that are responsible for production of highly internally excited products. In order to determine the nonadiabatic effect in the H + HBr reaction, Zare and coworkers [13] performed an experiment on the D + DBr (v = 0) reaction by the ion imaging method over a wide set of collision energies. However, no detectable spin-orbit excited Br\* atoms were found in their experiment, showing a very minor contribution of nonadiabatic channel for the D + DBr reaction. Therefore, they suggested that more experiments and calculations would be needed to understand how much the nonadiabatic transition affects this reaction. Recently, nonadiabatic dynamical calculations based on the new fitted diabatic potential energy surfaces by Han and coworkers [14] confirmed the experiment of Zare and coworkers.

On the theoretical side, many theoretical studies of both classical and quantum dynamics have been done for the BrH<sub>2</sub> system. Some years ago, Lynch et al. [15] constructed

a PES (denoted as e-LEPS) for the ground state ( $1^2 A'$ ) of the BrH<sub>2</sub> system, which is based on multireference configuration interaction (MRCI) calculations with a large basis set at the preselected 104 geometries. However, the barrier height was too high for the H + HBr abstraction reaction and its isotopic variants. To improve the accuracy of e-LEPS, Kurosaki and Takayanagi [16] constructed a global adiabatic PES (known as MB1) of the lowest three doublet states ( $1^2 A'$ ,  $2^2 A'$  and  $1^2 A''$ ) using the MRCI method including the Davidson's correction and SO coupling effects with the aug-cc-pVTZ basis set. Although thermal rate constants calculated with MB1 agree better with experiment than e-LEPS, they found that the absolute values of the *ab initio* energies for MB1 in the H + HBr asymptotic region did not converge and should be lowered by  $\sim 0.3$  kcal mol<sup>-1</sup>. Subsequently, the MB1 PES was modified to the MB2 [17] and MB3 [18] PESs which were obtained by recalculating the H + HBr asymptotic region using the same methodology as MB1. The rate constants on MB3 obtained with Fu and Zhang's [2] time-dependent quantum mechanical calculations are larger than the experimental values by a factor of 2 for temperatures up to 550 K, indicating that the MB3 PES should be improved to achieve better agreement between theory and experiment. For this purpose, Xie and co-workers [5] constructed a new PES of the ground state ( $1^2 A'$ ) for the H + HBr reaction based on the MRCI method including the Davidson's correction and SO coupling effects with the aug-cc-pVQZ basis set and a larger active space. The thermal rate constants calculated on the new PES using the time-dependent quantum mechanical calculations were in good agreement with the experimental values in a wide range of temperature. Moreover, Xie and co-workers [19] constructed the first set of diabatic PESs for the Br ( $^2P_{3/2,1/2}$ ) + H<sub>2</sub> reaction, and reported a dynamical study on their new coupled PESs to understand the nonadiabatic effect in the Br ( $^2P_{3/2,1/2}$ ) + H<sub>2</sub> reaction. Recently, in order to investigate the nonadiabatic effect in the H + HBr reaction (and other isotopic variants), Han and coworkers [14] have presented a new set of diabatic PESs based on a higher method.

In this work, we present the nonadiabatic quantum scattering calculations for the title reactions on the newly fitted PESs [14]. The organization of this paper is as follows: The nonadiabatic time-dependent wave packet method is briefly described in Section II. Section III presents the results and discussions of dynamical calculations. Finally, a short conclusion is made in Sec. IV.

## 2 Computational Details

The time-dependent wave packet method is the same as that used in earlier studies [20-27] and so shall be described briefly here. The total Hamiltonian for the atom-diatom in the reactant Jacobi coordinates ( $R, r, \theta$ ) can be expressed in atomic units as

$$\hat{H} = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + \frac{\hat{L}^2}{2\mu_R R^2} + \frac{\hat{j}^2}{2\mu_r r^2} + V(R, r, \theta) + V_{so}(R, r, \theta) + h(r) \quad (1)$$

The definitions of variables in Hamiltonian can be found in Ref. 28. The sum of the interaction potential and spin-orbit Hamiltonian can be written in the diabatic signed- $\lambda$  basis as follows:

$$V + V_{so} = \begin{bmatrix} & \langle \Sigma | & \langle \bar{\Sigma} | & \langle \Pi_1 | & \langle \bar{\Pi}_1 | & \langle \Pi_{-1} | & \langle \bar{\Pi}_{-1} | \\ & \lambda=0 & \lambda=0 & \lambda=1 & \lambda=1 & \lambda=-1 & \lambda=-1 \\ & \sigma=1/2 & \sigma=-1/2 & \sigma=1/2 & \sigma=-1/2 & \sigma=1/2 & \sigma=-1/2 \\ \langle \Sigma | & V_{\Sigma} & 0 & -V_1 & -\sqrt{2}B & V_1 & 0 \\ \langle \bar{\Sigma} | & 0 & V_{\Sigma} & 0 & -V_1 & -\sqrt{2}B & V_1 \\ \langle \Pi_1 | & -V_1 & 0 & V_{\Pi} - A & 0 & V_2 & 0 \\ \langle \bar{\Pi}_1 | & -\sqrt{2}B & -V_1 & 0 & V_{\Pi} + A & 0 & V_2 \\ \langle \Pi_{-1} | & V_1 & -\sqrt{2}B & V_2 & 0 & V_{\Pi} + A & 0 \\ \langle \bar{\Pi}_{-1} | & 0 & V_1 & 0 & V_2 & 0 & V_{\Pi} - A \end{bmatrix}$$

where  $V_{\Sigma} = V_{zz}$ ,  $V_{\Pi} = (V_{xx} + V_{yy})/2$ ,  $V_1 = V_{xz}/\sqrt{2}$ ,  $V_2 = (V_{yy} - V_{xx})/2$

The terms of  $V_{\Sigma}$ ,  $V_{\Pi}$ ,  $V_1$  and  $V_2$  are four diabatic PESs determined by the *ab initio* calculations [29-31], A and B are two components of the spin-orbit Hamiltonian matrix [32].

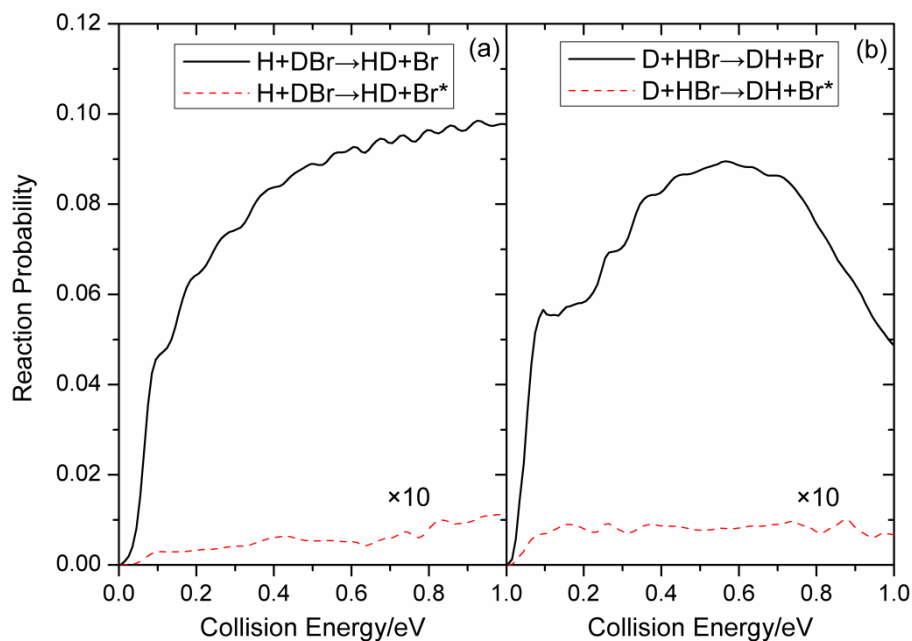
The time-dependent wave function can be expanded in terms of translational basis, vibrational basis and body-fixed total angular momentum eigenfunction. The split-operator method [21, 23] is employed to carry out the wave packet propagation on the multi-PESs. Finally, the initial state specified total probabilities are obtained by flux operator for each of electronic states, and the reaction cross section is obtained by summing the reaction probabilities over all partial waves (total angular momentum, J) [28]. Here, we ignored the Coriolis coupling effect because it is too expensive for us to carry out the rigorous Coriolis-coupled (CC) calculations on our coupled PESs for the title reactions.

The numerical parameters used in the dynamical calculation for the H + DBr reaction are as follows. We employed 220 sine functions (among them 130 for the interaction region) for the atom-diatom distance in a range of [1.5, 23.5] bohr, and 110 vibrational functions of DBr were employed for r coordinate in the range of [1.5, 12.5] bohr for the interaction region. The maximum rotational quantum number used is  $j_{max}=130$  to obtain the converged reaction probability. Five vibrational states are included in the asymptotic region. The average value of the translational energy, width, and center of initial wave packet are 0.5 eV and 0.25 bohr and 16.0 bohr. The wave packets are propagated for as long as 20000 a.u. (a

time step-size of 5 a.u. is used). In order to obtain the converged integral cross sections, more than 65 partial waves are calculated for the H + DBr reaction for the collision energy range 0-1 eV. The numerical parameters for the wave packet propagation for the D + HBr reaction are as follows. The translational and vibrational basis functions and R and r range are the same as that used in the H + DBr reaction. The maximum rotational quantum number used is  $j_{\max}=130$  to obtain the converged reaction probability. The maximum vibrational state is  $v_{\max}=5$  for DBr in the asymptotic region. The average value of the translational energy, width, and center of initial wave packet are 0.5 eV and 0.18 bohr and 16.0 bohr. The wave packets are propagated for as long as 20000 a.u. (a time step-size of 5 a.u. is used). To obtain the converged integral cross sections for the D + HBr reaction for the collision energy range here considered, we have calculated the reaction probabilities for a number of total angular momenta J up to 85.

### 3 Results and Discussion

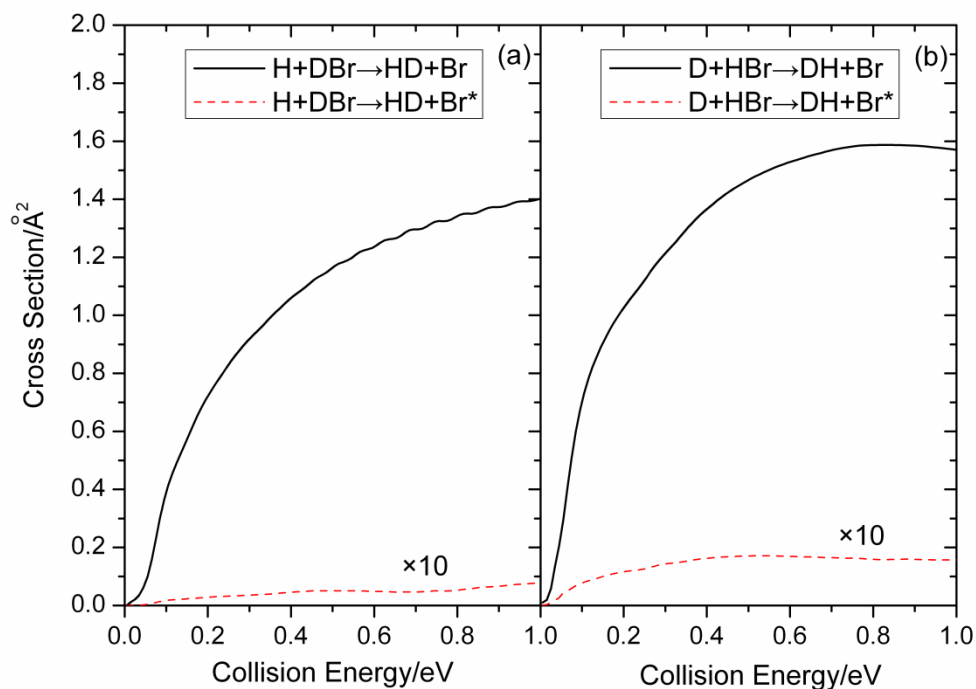
**Figure 1** shows the reaction probabilities for the H + DBr  $\rightarrow$  HD + Br (Br\*) reaction and D + HBr  $\rightarrow$  DH + Br (Br\*) reaction as a function of collision energy. First, one can see that the H + DBr  $\rightarrow$  HD + Br reaction and D + HBr  $\rightarrow$  DH + Br reaction do not show an energy threshold because of the very low barrier (only 0.066 eV) on the ground PES. As collision energy increases, the H + DBr  $\rightarrow$  HD + Br reaction probability increases rapidly in the collision energy range 0-0.1eV, then increases gradually as the collision energy increases further. According to the dynamics of H + HBr and D + DBr reaction, that is the collision energy hinders the ground abstraction reactivity in high-collision-energy range, we predict that the H + DBr  $\rightarrow$  HD + Br reaction probability begin to decreases at some collision energy as collision energy increases from 1eV to higher collision energies. We also present the reaction probability for the H + DBr  $\rightarrow$  HD + Br\* reaction in **Figure 1a**. For clarity, the result for the H + DBr  $\rightarrow$  HD + Br\* reaction is multiplied by 10. Even so, the result is still far less than that of the ground Br channel. This suggests that nonadiabatic effect only plays a minor role in the H + DBr reaction.



**Figure 1:** (a) Total reaction probabilities for the  $\text{H} + \text{DBr}(\nu_0 = 0, j_0 = 0) \rightarrow \text{HD} + \text{Br}(\text{Br}^*)$  reaction vs collision energy. For clarity, the results for the excited  $\text{Br}^*$  channel are multiplied by 10. (b) Same as (a) except for the  $\text{D} + \text{HBr}(\nu_0 = 0, j_0 = 0) \rightarrow \text{DH} + \text{Br}(\text{Br}^*)$  reaction.

As shown in **Figure 1b**, the reaction probability for the  $\text{D} + \text{HBr}$  ground channel increases gradually as the collision energy increases from 0.1 to 0.56 eV, however, it starts to decrease quickly from collision energy 0.7eV which is in qualitative agreement with the  $\text{H} + \text{HBr}$  reaction but different from the  $\text{H} + \text{DBr}$  reaction. We infer that the centrifugal barrier is responsible for this difference in the trend with collision energy. The  $\text{H} + \text{DBr} \rightarrow \text{HD} + \text{Br}$  reaction has larger centrifugal barrier than that of  $\text{D} + \text{HBr} \rightarrow \text{DH} + \text{Br}$  reaction. Likewise, we can draw the conclusion that the nonadiabatic effect only plays a minor role in the  $\text{D} + \text{HBr}$  reaction by comparing the two results in **Figure 1b**. On the other hand, **Figure 1** shows that the variation trends of the reaction probability for the ground Br channel and excited  $\text{Br}^*$  channel are quite different both for  $\text{H} + \text{DBr}$  and  $\text{D} + \text{HBr}$  reaction. The energy dependence of the reaction probability is possibly affected by the two factors. Firstly, the nonadiabatic transition is governed by the spin-orbit coupling and the energy difference between the electronic states. At high collision energy, more regions with larger energy difference between ground state and excited states are accessible. Thus, in addition to the  $\text{Br}(\text{Br}^*) + \text{HD}$  asymptotic region, the nonadiabatic transition may occur in the interaction region close to the product asymptotic region. Secondly, at any configuration of the PESs, more internal

states of  $\text{Br}^* + \text{HD}$  will open with the collision energy increasing.



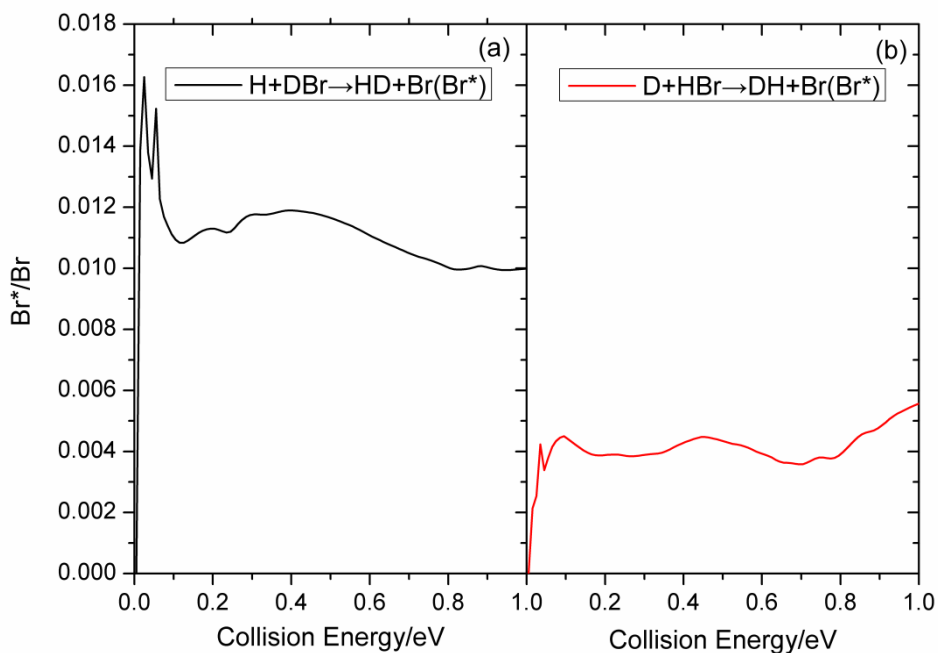
**Figure 2:** (a) Integral cross sections for the  $\text{H} + \text{DBr} (\nu_0 = 0, j_0 = 0) \rightarrow \text{HD} + \text{Br} (\text{Br}^*)$  reaction vs collision energy. For clarity, the results for the excited  $\text{Br}^*$  channel are multiplied by 10. (b) Same as (a) except for the  $\text{D} + \text{HBr} (\nu_0 = 0, j_0 = 0) \rightarrow \text{DH} + \text{Br} (\text{Br}^*)$  reaction.

**Figure 2** describes the integral cross sections (ICSs) for the  $\text{H} + \text{DBr} \rightarrow \text{HD} + \text{Br} (\text{Br}^*)$  reaction and  $\text{D} + \text{HBr} \rightarrow \text{DH} + \text{Br} (\text{Br}^*)$  reaction as a function of collision energy. First, due to the very low barrier (only 0.066 eV) of the ground PES, the ICSs of the  $\text{H} + \text{DBr} \rightarrow \text{HD} + \text{Br}$  reaction and  $\text{D} + \text{HBr} \rightarrow \text{DH} + \text{Br}$  reaction do not show an energy threshold. As the collision energy increases, the ICSs of the  $\text{H} + \text{DBr} \rightarrow \text{HD} + \text{Br}$  reaction and  $\text{D} + \text{HBr} \rightarrow \text{DH} + \text{Br}$  reaction increase steadily in the whole collision energy range we considered, that is in accordance with the  $\text{H} + \text{HBr}$  and  $\text{D} + \text{DBr}$  reaction. However, comparing **Figure 2** and **Figure 1**, the trend with collision energy is somewhat different for the  $\text{D} + \text{HBr} \rightarrow \text{DH} + \text{Br}$  reaction. This is because the result in **Figure 1** is the reaction probability for the  $J = 0.5$ , whereas the ICSs mainly depend on the larger  $J$  partial waves. Moreover, the reaction probabilities for the larger  $J$  are different from the result of the  $J = 0.5$  because of the increasing higher centrifugal barrier. The ICSs of the  $\text{H} + \text{DBr} \rightarrow \text{HD} + \text{Br}^*$  reaction and  $\text{D} + \text{HBr} \rightarrow \text{DH} + \text{Br}^*$  reaction are also presented in **Figure 2**. For clarity, the results for the excited  $\text{Br}^*$  channel are multiplied by 10. Even so, the results are still far less than that of the ground  $\text{Br}$  channel. In summary, we proved that the nonadiabatic effect only plays a minor

role in the H + HBr reaction (and other isotopic variants). On the other hand, the variation trends of the ICSs for the ground Br and excited Br\* channels are quite different both for the H + DBr and D + HBr reaction, and we have given some explanations in the preceding paragraph. The ICSs of the D + HBr reaction are larger than that of the H + DBr reaction. We deduce that the centrifugal barrier accounts for this difference. It turned out that the D + HBr reaction needs more partial waves to obtain the converged cross section. And we have tested that total angular momenta J up to 85 for D + HBr reaction are needed to obtain the converged ICSs, while J up to 65 are needed for the H + DBr reaction. In addition, we used centrifugal sudden (CS) approximation in our dynamical calculations; however, our results can give a reasonable estimation about the nonadiabatic dynamics in the title reactions. This follows the conclusion of Chu *et al.* on the F + H<sub>2</sub> reaction [33] that Coriolis coupling effect makes negligible contribution to the nonadiabatic dynamics of the excited state.

In order to give more quantitative discussions for the electronically nonadiabatic dynamics, we present the ratio of the ICS of the excited channel to the ground channel for the title reactions as a function of collision energy in **Figure 3**. First, the ratio does not show an energy threshold for both reactions, a result that we have interpreted in the above paragraphs. One can also see that there are resonance structures especially in the very low collision energy range, which are probably due to two factors. Firstly, it is the interference of the wave packets obtained from the ground PES during the nonadiabatic transition. Secondly, it is the transition from excited Br\* channel to ground Br channel in the product asymptotic region. The ratio of H + DBr reaction is larger than that for D + HBr reaction by a factor of about two. In view of our last report [14], that the nonadiabatic effect in the H + HBr reaction is larger than that in the D + DBr, it seems that the nonadiabatic effect is inversely proportional to the triatomic reduced mass. Above all, the ratio is less than 0.016 for collision energies up to 1.0 eV for the two reactions; therefore, the nonadiabatic effect is negligible for the title reactions in the energy range here considered. To sum up, the nonadiabatic effect is negligible for the H + HBr reaction (and other isotopic variants).





**Figure 3:** The ratio of the ICS of the excited channel to the ground channel for the H + DBr and D + HBr reaction as a function of collision energy.

## 4 Conclusion

Nonadiabatic time-dependent wave packet calculations have been carried out on the newly fitted PESs for the H + DBr and D + HBr reactions. Reaction probabilities and integral cross sections are calculated for the collision energy up to 1.0 eV. Our results show that the nonadiabatic effect is negligible for the title reactions in the energy range here considered. In summary, the nonadiabatic effect is negligible for the H + HBr reaction (and other isotopic variants), and the Born-Oppenheimer approximation is invaluable in the application of quantum mechanics to the H + HBr reaction (and other isotopic variants).

## Acknowledgments

We thank Dalian Branch of Supercomputing Center of Chinese Academy of Sciences for computing support.

## References

- [1] T. J. Mitchell, A. C. Gonzalez, and S.W. Benson, Very Low Pressure Reactor Study of the  $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$  Reaction, *J. Phys. Chem.*, 99 (1995), 16960-16966.
- [2] B. Fu and D. H. Zhang, A Time-Dependent Quantum Dynamical Study of the  $\text{H} + \text{HBr}$  Reaction, *J. Phys. Chem. A*, 111 (2007), 9516-9521.
- [3] A. N.Panda and S. C. Althorpe, Quantum wave packet study of the  $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$  reaction, *Chem. Phys. Lett.*, 439 (2007), 50-54.
- [4] W. Q. Zhang, S. L. Cong, C. H. Zhang, X. S. Xu, and M. D. Chen, Theoretical Study of Dynamics for the Abstraction Reaction  $\text{H}' + \text{HBr}(v = 0, j = 0) \rightarrow \text{H}'\text{H} + \text{Br}$ , *J. Phys. Chem. A*, 113 (2009), 4192-4197.
- [5] B. Jiang, C. J. Xie, and D. Q. Xie, New ab initio potential energy surface for  $\text{BrH}_2$  and rate constants for the  $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$  abstraction reaction, *J. Chem. Phys.*, 134 (2011), 114301-1-9.
- [6] A. E. Pomerantz, J. P. Camden, A. S. Chiou, F. Ausfelder, N. Chawla, W. L. Hase, and R. N. Zare, Reaction products with internal energy beyond the kinematic limit result from trajectories far from the minimum energy path: an example from  $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$ , *J. Am. Chem. Soc.*, 127 (2005), 16368-16369.
- [7] T. Takayanagi and Y. Kurosaki, Quantum scattering calculations for the electronically nonadiabatic  $\text{Br}(^2\text{P}_{1/2}) + \text{H}_2 \rightarrow \text{H} + \text{HBr}$  reaction, *J. Chem. Phys.*, 113 (2000), 7158-7164.
- [8] W. L. Quan, Q. Song, and B. Y. Tang, The effects of the rotational excitation on the  $\text{Br} + \text{H}_2$  reaction and its dependence on the potential energy surfaces, *Chem. Phys. Lett.*, 442 (2007), 228-232.
- [9] W. L. Quan, Q. Song, and B. Y. Tang, Quantum scattering calculation for  $\text{Br} + \text{H}_2$  reaction on a new ab initio potential energy surface, *Chem. Phys. Lett.*, 437 (2007), 165-169.
- [10] W. L. Quan, P. Y. Tang, and B. Y. Tang, Quantum Scattering Calculation for Reaction  $\text{Br} + \text{H}_2$  on Two Potential Energy Surfaces, *Int. J. Quantum Chem.*, 107 (2007), 657-664.
- [11] E. S. Campbell and R. M. Fristrom, Reaction Kinetics, Thermodynamics, And Transport In The Hydrogen-Bromine System - A Survey Of Properties For Flame Studies, *Chem. Rev.*, 58 (1958), 173-234.
- [12] D. J. Nesbitt and S. R. Leone,  $\text{Br}^*(^2\text{P}_{1/2}) + \text{H}_2$  ( $v = 0, 1$ ): Laser studies of the competition between reactive pathways and inelastic energy transfer channels, *J. Chem. Phys.*, 73 (1980), 6182-6190.
- [13] J. Y. Zhang, J. Jankunas, N. C. M. Bartlett, N. T. Goldberg, and R. N. Zare, Search for  $\text{Br}^*$  production in the  $\text{D} + \text{DBr}$  reaction, *J. Chem. Phys.*, 132 (2010), 084301-1-7.
- [14] A.J. Zhang, P.Y. Zhang, T.S. Chu, K.L. Han and G.Z. He, Quantum dynamical study of the electronic nonadiabaticity in  $\text{D} + \text{DBr} \rightarrow \text{Br}(\text{Br}^*) + \text{D}_2$  reaction on new diabatic potential energy surfaces, *J. Chem. Phys.*, 137 (2012), 194305-1-6.
- [15] G. C. Lynch, D. G. Truhlar, F. B. Brown, J.-G. Zhao, A new potential energy surface for  $\text{H}_2\text{Br}$  and its

- use to calculate branching ratios and kinetic isotope effects for the H + HBr reaction, *J. Phys. Chem.*, 99 (1995), 207-225.
- [16] Y. Kurosaki and T. Takayanagi, Global ab initio potential energy surfaces for the lowest three doublet states ( $1^2 A'$ ,  $2^2 A'$  and  $1^2 A''$ ) of the BrH<sub>2</sub> system, *J. Chem. Phys.*, 119 (2003), 7838-7856.
- [17] Y. Kurosaki and T. Takayanagi, A modified version of the analytical potential function for the global ab initio ground-state potential energy surface of the BrH<sub>2</sub> system, *Chem. Phys. Lett.*, 406 (2005), 121-125.
- [18] Y. Kurosaki and T. Takayanagi, Private communication.
- [19] B. Jiang, C. J. Xie, and D. Q. Xie, New ab initio coupled potential energy surfaces for the Br( $^2P_{3/2}$ ,  $^2P_{1/2}$ ) + H<sub>2</sub> reaction, *J. Chem. Phys.*, 135 (2011), 164311-1-9.
- [20] Y. Zhang, T. X. Xie, K. L. Han and J. Z. H. Zhang, Time-dependent quantum wave packet calculation for nonadiabatic F( $^2P_{3/2}$ ,  $^2P_{1/2}$ ) + H<sub>2</sub> reaction, *J. Chem. Phys.*, 119 (2003), 12921-12925.
- [21] T. X. Xie, Y. Zhang, M. Y. Zhao, K. L. Han, Calculations of the F + HD reaction on three potential energy surfaces, *Phys. Chem. Chem. Phys.*, 5 (2003), 2034-2038.
- [22] P. Y. Zhang, R.F. Lu, T.-S. Chu and K.-L. Han, Quenching of OH ( $A^2\Sigma^+$ ) by H<sub>2</sub> through conical intersections: Highly excited products in nonreactive channel, *J. Phys. Chem. A*, 114 (2010), 6565-6568.
- [23] T. S. Chu, Y. Zhang and K. L. Han, The time-dependent quantum wave packet approach to the electronically nonadiabatic processes in chemical reactions, *Int. Rev. Phys. Chem.*, 25 (2006), 201-235.
- [24] R. F. Lu, T. S. Chu, Y. Zhang, K. L. Han, A. J. C. Varandas, and J. Z. H. Zhang, Nonadiabatic effects in the H + D<sub>2</sub> reaction, *J. Chem. Phys.*, 125 (2006), 133108-1-6.
- [25] H. Yang, M. Hankel, A.J.C. Varandas, K.L. Han, Nonadiabatic quantum dynamics calculations for the N + NH → N<sub>2</sub> + H reaction, *Phys. Chem. Chem. Phys.*, 12 (2010), 9619-9623.
- [26] S.J. Lv, P.Y. Zhang, K.L. Han and G. Z. He, Exact quantum scattering study of the H + HS reaction on a new ab initio potential energy surface H<sub>2</sub>S( $^3A$ ), *J. Chem. Phys.*, 136 (2012), 094308-1-7.
- [27] H. S. Zhai and K.L. Han, New ab initio potential energy surface and quantum dynamics of the reaction H( $^2S$ ) + NH( $X^3\Sigma^-$ ) → N( $^4S$ ) + H<sub>2</sub>, *J. Chem. Phys.*, 135 (2011), 104314-1-7.
- [28] J. Z. H. Zhang, *Theory and Application of Quantum Molecular Dynamics*; World Scientific: Singapore, 1999.
- [29] MOLPRO, a package of ab initio programs designed by H.-J. Werner and P.J. Knowles, version 2006.1, R. D. Amos, A. Bernhardsson, A. Berning, et al. (see <http://www.molpro.net>)
- [30] M. H. Alexander, Adiabatic and approximate diabatic potential energy surfaces for the B...H<sub>2</sub> van der waals molecular, *J. Chem. Phys.*, 99 (1993), 6014-6026.
- [31] M. H. Alexander, D. E. Manolopoulos and H. J. Werner, An Investigation of the F + H<sub>2</sub> Reaction Based on a Full Ab Initio Description of the Open-Shell Character of the F( $^2P$ ) Atom, *J. Chem. Phys.*, 113 (2000), 11084-11100.

- [32] A. Berning, M. Schweizer, H.-J. Werner, P. J. Knowles and P. Palmieri, Spin-orbit matrix elements for internally contracted multireference configuration interaction wavefunctions, *Mol. Phys.*, 98 (2000), 1823-1833.
- [33] T.S. Chu and K.L. Han, Effect of Coriolis coupling in chemical reaction dynamics, *Phys. Chem. Chem. Phys.*, 10 (2008), 2431-2441.