Time-dependent wave-packet quantum scattering study of the reactions $D^-+H_2\rightarrow H^-+HD$ and $H^-+D_2\rightarrow D^-+HD$

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The cross sections of the title reactions were calculated as functions of collision energy in the range 0.2–2.4 eV on a potential energy surface of Panda and Sathyamurthy [J. Chem. Phys. **121**, 9343 (2004)]. The calculated results with the Coriolis coupled method were found to be more consistent with the experimental ones than the centrifugal sudden approximation, thus suggesting that Coriolis coupling plays an important role in those reactions. A pronounced isotopic effect was also revealed and attributed to the significant difference of the effective potential barrier height in both reactions.

I. INTRODUCTION

Being a typical ion-molecule reaction, H^-+H_2 and its isotopic reactions are of interest in understanding the collision processes in interstellar media, the plasmas, and high-energy physics studies [1–3]. There have been a number of the experimental and theoretical studies on the electronic structure of H_3^- and its isotopic systems [4–22]. Recently, by using the tandem mass spectrometer (TMS), Michels and Paulson [4] measured the reaction cross section for collisions of H^- and D^- with H_2, D_2, and HD, and Huq *et al.* [5] measured the total reaction cross sections for the reactive and the electron detachment channels. The integral reaction cross section for (H^-, D_2) collisions was determined by Zimmer and Linder [6] with the crossed beam techniques. And they observed that the decrease in reaction cross section, when plotted as a function of collision energy, arose at higher energies due to the opening up of the electron detachment channel. Using a guided beam apparatus, Haufler *et al.* [7] determined the integral cross sections for H^-+D_2 and D^-+H_2 reactions and the pronounced isotope effect was found in the experiment.

Remarkable progress on molecular reaction dynamics calculations has been made in recent years due partly to the ability of determining accurate potential energy surface (PES) from *ab initio* quantum calculations for simple reactive systems. The differential and integral cross sections were calculated by Gianturco and Kumar [8] for vibrationally inelastic processes in (H^-+H_2) collisions over collision energy (4.67–40 eV) on the Stärck and Meyer (SM) PES.

In the previous papers, Coriolis coupling effect is shown to be significant in both the nonadiabatic and the adiabatic reactions of the ion-molecule collisions of D^++H_2 [20] and $He+H_2^+$ [24] as well as H^-+D_2 [1]. In this paper, using the recent *ab initio* PES of Panda and Sathyamurthy (PS) [11] and time-dependent wave-packet quantum method, we have carried out $D^-(\nu=0;j=0)+H_2\rightarrow H^-+DH$ and $H^-(\nu=0;j=0)+D_2\rightarrow D^-+HD$ in the collision energy range of 0.2–2.4 eV with the Coriolis coupling (CC). The present ex-

act CC result [12,13] from the ground rotational state $j=0$ will provide further physical insights into the reaction mechanism. To assess the influence of the CC on the reaction system, we have also performed the centrifugal sudden (CS) approximation calculations. We outline the theoretical methodology briefly in Sec. II, and the results obtained are presented and discussed in Sec. III. A summary of our findings and the conclusion follow in Sec. IV.

II. THEORETICAL METHOD

The time-dependent wave-packet (TDWP) method [14] has been widely used in dynamical studies for elucidation of the mechanism of reactive systems. With the split-operator propagator scheme, the methods were used to numerically solve the time-dependent Schrödinger equation of the reactive system. Including CC and invoking the Born-Oppenheimer approximation, in the reactant Jacobi coordinates, the Hamiltonian of the H_2D^-/D_2H^- reactive system can be expressed as

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

where R and r have their usual definitions in Jacobi coordinates [14,23]; μ_R and μ_r are corresponding reduced masses [14]; $\hat{J}$ and $\hat{j}$ are the total angular momentum and the rotational angular momentum of H_2/D_2, respectively; $V(\hat{R},\hat{r})$ is the potential energy surface of PS; and $h(r)$ is the diatomic reference Hamiltonian

$$h(r) = -\frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} + V(r). \quad (2)$$

Here, $V(r)$ is the diatomic reference potential.

The time-dependent wave function can be expanded in terms of the body-fixed (BF) translational basis $U_n^v(R)$, the vibrational basis $\phi_v(r)$, and total angular momentum eigenfunction rotational basis functions $Y_{jK}^{JM\varepsilon}(\hat{R},\hat{r})$ using the reactant Jacobi coordinates [14,23]. The following parameters
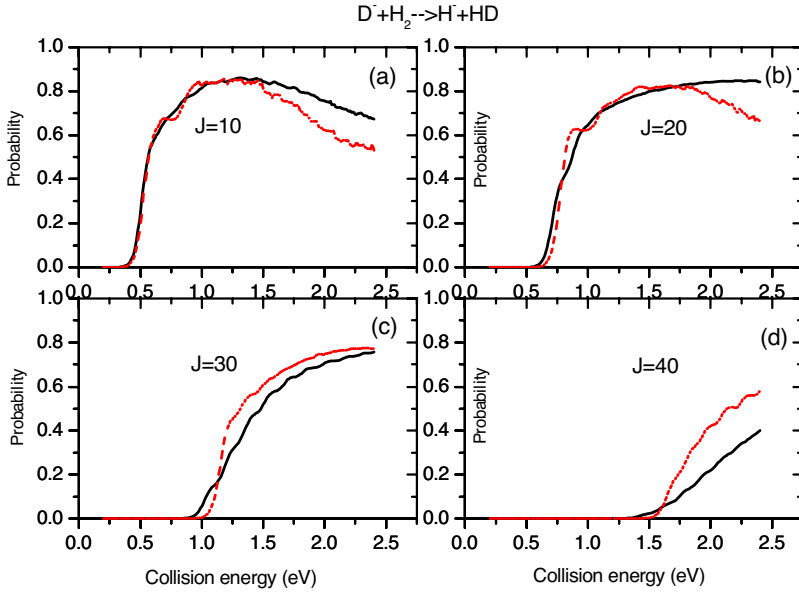
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FIG. 1. (Color online) A comparison between the CC and CS probabilities in the collision energy range of 0.2–2.4 eV for initial quantum numbers $j=0$, $v=0$, $k_0=0$, and for total angular momentum (a) $J=10$, (b) $J=20$, (c) $J=30$, and (d) $J=40$.

were used to get the converged results: 358 translational basis functions for the R coordinate in the range of 0.1–40.0 a.u., 100 vibrational basis functions for the r coordinate of 0.2–12.06 a.u., $j_{max}=80$ for rotational basis functions, and a propagation time of 60 000 a.u. The number of K that is the quantum number for the body-fixed z component of the angular momentum used in the CC calculations is up to nine. The proper parameters were used to get the converged results.

The matrix obtained by applying the centrifugal potential operator $(\hat{J}-\hat{j})^2/2\mu_R R^2$ on the rotational basis functions $Y_{jK}^{JM\varepsilon}(\hat{R},\hat{r})$ is diagonal in the CS approximation calculation [15,16], while in the CC calculation [12,13,25] different K states coupled with each other and constituted the off-diagonal elements of the matrix.

The initial wave function is propagated by a split-operator method [17]; the total reaction probability and the integral reaction cross sections can be calculated by [14]

$$P_{j_0 k_0 v_0}^J(E) = \frac{\hbar s}{\mu_r} \operatorname{Im}[\langle\psi(E)|\delta(r-r_0)|\psi(E)\rangle], \quad (3)$$

$$\sigma_{j_0 k_0 v_0}(E) = \frac{\pi}{k^2}\sum_J (2J+1)P_{j_0 k_0 v_0}^J(E), \quad (4)$$

$$\sigma_{j_0 v_0}(E) = \frac{1}{2j_0+1}\sum_{k_0}\sigma_{j_0 k_0 v_0}(E), \quad (5)$$

where $\psi(E)$ is the corresponding time-independent part of the final wave function, k is the wave number corresponding to the initial state at a fixed collision energy E. The reader can refer to Refs. [10–18] for more detailed of the methodology and parameter.

III. RESULTS AND DISCUSSION

Figures 1(a)–1(d) show the CC and CS probabilities for ground state and the total angular momentum $J=10, 20, 30,$

40, respectively, in the collision energy range of 0.2–2.4 eV, and all the following results of this work are in the same energy range. It can be seen that trend of the lines, the values themselves, and the threshold energy in the calculated probabilities are quite different for the two sets of calculations, except Fig. 1(a). For low J values, such as $J=10, 20$, the CC and CS probabilities are almost the same in the low energy, while the values of CC is larger than the CS in the high energy; But as J becomes larger, for example, $J=30$ and 40, the differences are observed in that the CC values are smaller than the CS values in the high energy.

Figures 2(a) and 2(b) show the probabilities of D^-+H_2 [Fig. 2(a)] and H^-+D_2 [Fig. 2(b)] in the collision energy range of 0.2–2.4 eV for $j=0$, $v=0$, and the total angular momentum $J=10, 20, 30,$ and 40, individually. The CC was included in the calculation for $J=10, 20, 30,$ and 40, as indicated by solid line, dashed line, dotted line, dash-dotted line, respectively. The threshold increases with the increase of J.

In Fig. 3, the calculated cross section is presented on the PS PES for collision of D^- with H_2. The cross sections include the summation of reaction probabilities continuous J values (up to 65). The curves of the total reaction cross sections $\sigma_{j_0 v_0}(E)$ for the CC and CS calculations differ significantly in the higher collision energy. As can be seen in Fig. 3, the CS is larger than the CC cross section in the collision energies; larger than 0.8 eV with a maximum difference of $\approx 10\%$ at the collision energy of 1.87 eV, the cross point exists in the investigated collision energy range. Due to the J-averaging effect, some resonances observed in the probability curves of Figs. 1 and 2 are greatly washed out in the CC and CS cross sections shown in Fig. 3. On the other hand, clearly it shows that the CC results in this work are closer to the experimental results by Haufler *et al.* [7] than the others, but the CC results in this work are smaller than the experimental results in the low energy and bigger than the experimental results in the high energy; the difference is also pronounced. Some kinds of excited states were included in the experiment, while only the $v=0$, $j=0$, $k_0=0$ states
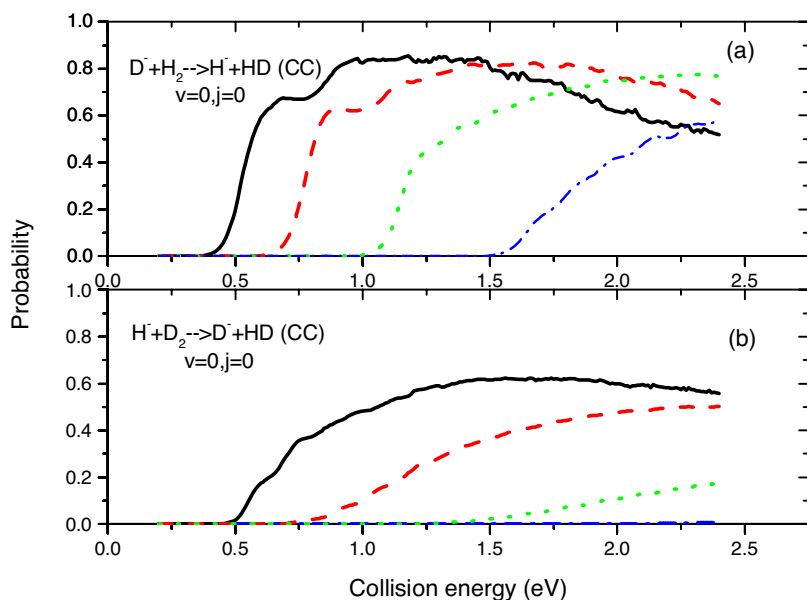
FIG. 2. (Color online) The probabilities of D^-+H_2 (a) and H^-+D_2 (b) in the collision energy range of $0.2-2.4$ eV for $j=0$, $\nu=0$, $k_0=0$, and CC was included in the calculation and for the total angular momentum $J=10$, 20, 30, and 40, for solid line, dashed line, dotted line, dash-dotted line respectively.

were considered in our calculation. So it is reasonable that our theoretical CC results were much bigger than the experimental results in the high energy. The trend of the CS results and the CC results is slightly different in the cross sections. For the centrifugal sudden approximations included in the CS results, the threshold of CC is a little lower than the CS results. Our results are bigger than the cross sections calculated by Michels and Paulson [4] because they carried out the calculations on a different potential energy surface than we did, which was constructed using an optimized double-zeta-plus-polarization-and-diffuse-orbital Slater-type orbital

(STO) basis set within a configuration-interaction valence bond framework made by themselves [4]. But in the whole energy range, our results are much lower than the theoretical CS results of Panda *et al.* [2], although the same PES was used in both calculations. However, for both calculations, the individual reaction probabilities of $J=0$, 10, 20, 30, and 40 are almost the same.

The cross section results of H^-+D_2 is presented in Fig. 4 as a function of collision energy in the range of $0.2-2.4$ eV. As can be seen in Fig. 4, the CS cross section is larger than the CC cross section in the collision energy range. A maximum difference of more than 20% is found at the collision energy of 1.62 eV, the cross point also exists in the investi-
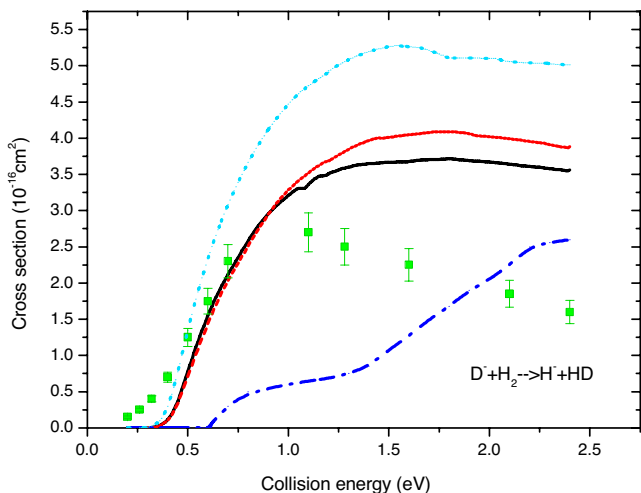

FIG. 3. (Color online) A comparison between the CC and CS cross sections in this work for $D^-+H_2 \rightarrow H^-+HD$ reaction in the collision energy range of $0.2-2.4$ eV for $j=0$, $\nu=0$, and $k_0=0$. Comparison is carried out between the experimental cross sections of Haufler *et al.*, which is notated by the small solid square in Å^2 and other results [7]. And the solid line and the dashed line represent the present CC and CS cross sections of this work, respectively. The dash-dotted line is the theoretical results of Michels and Paulson [4], and the dotted line is the theoretical result of Panda, Giri, and Sathyamurthy [2].
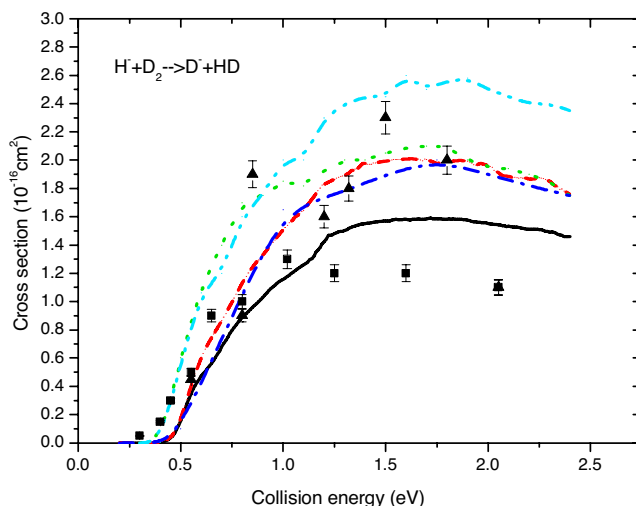

FIG. 4. (Color online) A comparison between the CC (solid line) and CS (dashed line) cross sections for $H^-+D_2 \rightarrow D^-+HD$ reaction in the collision energy range of $0.2-2.4$ eV for $j=0$, $\nu=0$, and $k_0=0$. The theoretical cross section in Å^2 by Morari and Jaquet [1] is for the dotted line with CC included. The dash-dotted line is for Panda *et al.* [2] in CS. Dash-dot-dotted line is for Morari and Jaquet [1] in CS, and the experimental results of Haufler *et al.* [7] for the solid square and of Zimmer and Linder [6] for solid triangle.

gated collision energy range. Much difference was also found in the CC and CS results of Morari and Jaquet [1]. As one can see from Fig. 4, the CS results in this work are almost the same as the CS results of Panda *et al.* on the PS PES [2], while a big difference was found when we compared our results with those of Morari and Jaquet [1]. This may be because the integral cross sections are empirically estimated by using the *J*-shift approach in Ref. [1]. The overall behavior of the theoretical results in this work fits well with the guided-beam measurements of Haufler *et al.* [7] and also in the chemical precision comparison with the crossed-beam measurements of Zimmer and Linder [6]. The most agreement with the experimental results of Haufler appears in the CC results.

From Figs. 3 and 4, we can see that in this work the CC cross section increases sharply at the threshold followed by a maximum value and then a slight decline. The CS result is higher than the CC result in the high energy for the negligence of the Coriolis coupling. Indeed, now the conjecture of Panda and Sathyamurthy [2] was confirmed by the different results of the present CC and CS calculations in explaining the discrepancies between the experimental data and the quantum-calculated CS cross sections. On the basis of the above comparison, we conclude that significant differences exist between the CC and CS calculated results, especially with respect to high energy.

Interestingly, the importance of Coriolis coupling was also revealed for some ion-molecule reactions [20,24] in the recent quantum wave-packet study. The preceding comparison and explanation have highlighted the important role of the Coriolis coupling for an accurate scattering calculation. As pointed out by McLenithan and Secrest [18], Thachuk and McCourt [19] separately studied the CS approximation and artificially hindered the collision-induced orientation changes in the molecular angular momentum vector [18]; therefore, it works with sudden collision, but the fact that collisions do not occur suddenly may lead to the failure of the CS approximation in describing the dynamical behaviors of the present system. Although more tests are still needed to answer whether the CC would generally play a similarly important role in other ion-molecule reaction systems, now the CS approximation should be used with caution in quantum-scattering studies of ion-molecule reactions in the future [24].

The cross sections of H^-+D_2 and D^-+H_2 are compared in Fig. 5 as functions of collision energy in the range of 0.2–2.4 eV and the CC is included. In Fig. 5, both curves in this work were calculated of the $j=0$, $v=0$, $k_0=0$ states on the PS PES. The general trend observed for the two isotopic variants curve is in very similar, as expected. However, the fact that the cross section for the D^-+H_2 reaction (heavy ion colliding with the light molecule) is larger by a factor of more than two times than that of the reaction H^-+D_2. This large isotope effect is the same as the experimental results of Haufler *et al.* reported in Ref. [7], and also reported by Huq *et al.* in Ref. [5]. The solid square is for reaction D^-+H_2, and the solid triangle is for the reaction H^-+D_2, both experimental results are given by Haufler *et al.* [7]; the isotope effect
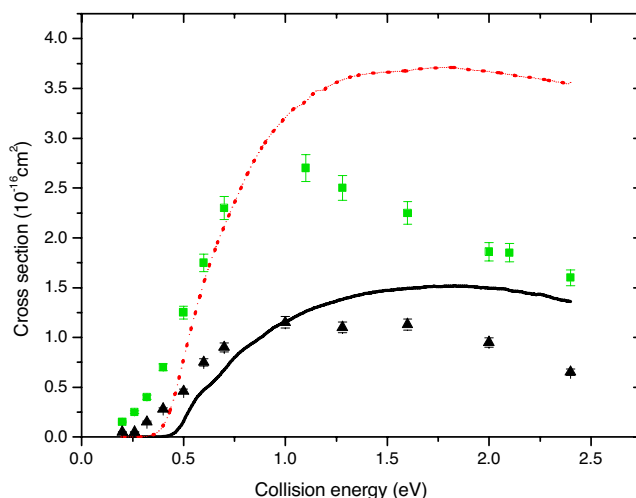

FIG. 5. (Color online) A comparison between the cross section of reaction H^-+D_2 and the reaction of D^-+H_2 in the collision energy range of 0.2–2.4 eV in the initial ground state including the CC on the PS PES, and the solid line is of the reaction H^-+D_2 cross section and the dashed line is of D^-+H_2. The solid square is for the experimental results of reaction D^-+H_2, and the solid triangle is for H^-+D_2 by Haufler *et al.* reported in Ref. [7].

was pronounced, just as in the results of Huq *et al.* [5].

The major reason for the striking isotopic effect is due to the increased reactivity of D^-+H_2 found in the dynamics for the entrance channel. The differences in thresholds were observed in the detachment channels for H^- and D^- in the present studies. The cross section for H^- production reaction process was observed to be much larger than that for D^- production over the entire energy range investigated. It is possible that these large isotopic effects are mainly related to the announced difference of the effective potential barrier height (the summary of the classical potential barrier height and the zero-point energies) between $D^-+H_2 \rightarrow HD+H^-$ reaction (effective barrier height 0.48081 eV) and $H^-+D_2 \rightarrow HD+D^-$ reaction (effective barrier height 0.49973 eV).

IV. CONCLUSIONS

We have carried out a three-dimensional time-dependent wave-packet scattering calculation for the initial state-selected reaction $D^-+H_2 \rightarrow H^-+HD$ and $H^-+D_2 \rightarrow D^-+HD$ in the collision energy range of 0.2–2.4 eV on the PS PES. Comparing the CS approximation results with those including CC, the CC results show an improvement, which is closer to the experimental results of Haufler *et al.* and other experimental results. This observation supports the conclusion that for an accurate scattering calculation on the present ion-molecule reaction, it is necessary to include the Coriolis coupling. The isotopic effect was very pronounced, due to the big difference in the effective potential barrier height.

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