

COMMUNICATION

Effects of the reagent vibrational excitation on the stereodynamics of the reaction $C(^3P) + CH(X^2\Pi) \rightarrow C_2 + H$

Jia Liu, Meishan Wang*, Chuanlu Yang, Mingxin Wang, Xiaolin Sui, Zhenhua

Gao

**School of Physics and Optoelectronics Engineering, Ludong University, Yantai 264025, China*

Received 15 Dec 2014; Accepted (in revised version) 6 Jan 2015

Abstract: Based on the $1^2A''$ global three-dimensional adiabatic potential energy surface [Boggio- Pasqua et al., Phys Chem. Chem. Phys 2:1693 2000], a theoretical study of the stereodynamics of the reaction $C(^3P) + CH(X^2\Pi)(v = 0 - 6, j = 0)$ has been performed using the quasi-classical trajectories (QCT) method. The cross sections as a function of the reagent vibrational quantum number are presented. The differential cross sections (DCSs) and the distributions of $P(\theta_r)$, $P(\phi_r)$ at the selected collision energy of 0.3eV are discussed in detail. Through the study of reaction trajectories, the change of reaction mechanism is revealed. The product rotational alignment parameter $\langle P_2(j \cdot k) \rangle$ are also obtained as a function of the reagent vibrational quantum number. The calculated results show that the reagent vibrational excitation plays an important role in the title reaction.

AMS subject classifications: 81U10, 81V45

Keywords: Stereodynamics; QCT method; Vibration excitation; Rotational alignment; Reaction mechanism

The ethanol radical C_2H is one of the most abundant polyatomic species in carbon-rich stars and interstellar clouds [1, 2]. C_2H is believed to be the major source of C_2 in comets and interstellar media [3-6]. It is also the simplest organic triatomic molecule involving a triple $C \equiv C$ bond and has a low-lying electronic state. Moreover, C_2H plays an important role in the formation and the destruction of carbon chain molecules C_2H_n (with $n=2-6$) [7]. The C_2H radical is not only the product of some reactions like $C_2 + CH_4$ [8], $H_2 + CH_4$ [9] and the photo dissociation of acetylene [10], but also an important intermediate species of numerous

* Corresponding author. E-mail address: mswang1971@163.com (M. S. Wang). Tel./fax: +86 535 6672142.
<http://www.global-sci.org/cicc>

combustion reactions [3, 11].

More recently, Boggio-Pasqua and co-workers [2] build an analytical representation of the three lowest adiabatic potential energy surfaces which correspond to the states $X^2\Sigma^+$ and $A^2\Pi$ of C_2H [11,12]. These three surfaces belong to the $^2A'$ or $^2A''$ symmetry species [2, 11, 12]. In 2001, Tang et al. calculated the dynamics of the title reaction by using a quantum time-dependent wave packet method on the $1^2A'$ and $2^2A'$ surface [2, 11]. In 2010, Yang et al. studied the effect of initial rotational quantum number on the $1^2A'$ surface [13]. As far as we know, the most theoretical studies are based on the $1^2A'$ and $2^2A'$ PES and the calculated results conform the accuracy of these PES [11-18]. However, there are only three reports on properties of its vector properties about this reaction on $1^2A''$ PES [19-21]. Zhang et al. found the cross sections and the value of $\langle P_2(j' \cdot k) \rangle$ of the title reaction decrease with the increase of collision energy [19]. Liu et al. reported the product C_2 is mainly backward-forward scattering and the orientation of the product rotational angular momentum tends to point to the negative direction of the y -axis at $E_{col}=0.1\text{eV}$ on the $1^2A''$ PES [20]. Wu et al. discovered that the title reaction performed a preference of forward scattering and a weak of product rotation alignment considering isotopic effect of CH [21]. To shed more light on the dynamics of this reaction, we apply the QCT method [22-26] to study the effects of reagent vibrational excitation on the stereodynamics of the $C(^3P) + CH(X^2\Pi)(v = 0 - 6, j = 0) \rightarrow C_2 + H$ reaction based on the $1^2A''$ PES [2].

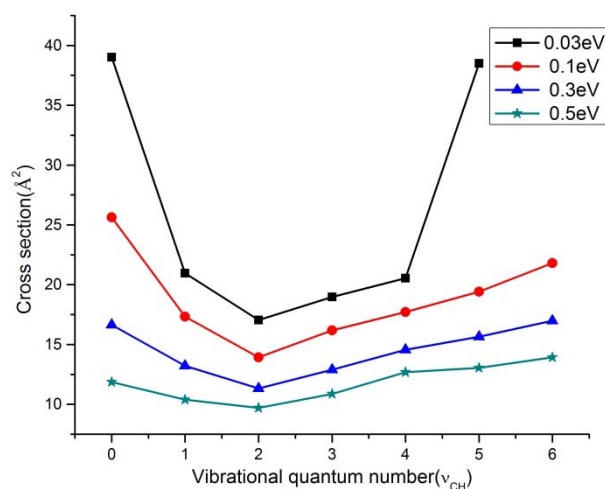


Figure 1: Total reaction cross section for $C(^3P) + CH(X^2\Pi)(v = 0 - 6, j = 0) \rightarrow C_2 + H$ as a function of v at different collision energies.

Figure 1 shows the influence of the initial reagent vibrational excitation on the reaction cross sections for $C(^3P) + CH(X^2\Pi)(v = 0 - 6, j = 0)$ at the relative collision energies $E_{col} =$

0.03, 0.1, 0.3, 0.5eV, respectively. Regardless the reagent vibrational excitation, it is easy to conclude that the reaction cross sections decrease with the increase of the collision energies, which is due to no energy barriers on the PES of the title reaction. For the given collision energy, it can be seen that the values of cross section decrease when the vibrational quantum number changes from $v=0$ to $v=2$ and then evidently increase when v further increases from $v=2$ to $v=6$. The decreasing-then-increasing trend suggests that the reaction intensity firstly becomes weaker and then stronger as increasing the vibrational quantum number of CH. This phenomenon can occur in each of the four collision energies.

Table 1: The impact parameters $b_{\max}$ for $C(^3P) + CH(X^2\Pi)(v = 0 - 6, j = 0)$ at $E_{\text{col}}=0.03, 0.1, 0.3, 0.5$ eV

v_{CH}	0	1	2	3	4	5	6
$b_{\max}(\text{\AA})$ ($E_{\text{col}}=0.03\text{eV}$)	5.120	4.420	4.350	4.380	4.550	5.330	-
$b_{\max}(\text{\AA})$ ($E_{\text{col}}=0.1\text{eV}$)	4.102	4.018	3.976	3.975	3.997	4.085	4.250
$b_{\max}(\text{\AA})$ ($E_{\text{col}}=0.3\text{eV}$)	3.667	3.631	3.605	3.680	3.895	4.175	4.355
$b_{\max}(\text{\AA})$ ($E_{\text{col}}=0.5\text{eV}$)	3.479	3.455	3.520	3.734	3.930	4.150	4.270

To explain the above phenomenon, we investigated the effect of different collision energies and vibrational excitation on the maximum impact parameters and reaction probability, which are displayed in **Table 1** and **Table 2**, respectively. It could be surprise that the values of $b_{\max}$ and the reaction probability take on the same change trend as the cross section at each of the four collision energies. In other words, with the increase of the vibrational quantum number, the maximum impact parameters and reaction probability present the decreasing-then-increasing trend. This trend contributes to the change of cross sections. In order to simplify the calculation process, we selected the collision energy $E_{\text{col}}=0.3\text{eV}$.

Table 2: The reaction probability p for $C(^3P)+CH(X^2\Pi)(v=0-6, j=0)$ at $E_{\text{col}}=0.03, 0.1, 0.3, 0.5$ eV

v_{CH}	0	1	2	3	4	5	6
p ($E_{\text{col}}=0.01\text{eV}$)	0.4737	0.3417	0.2868	0.3150	0.3160	0.4314	-
p ($E_{\text{col}}=0.1\text{eV}$)	0.4849	0.3481	0.2804	0.3259	0.3531	0.3702	0.3844
p ($E_{\text{col}}=0.3\text{eV}$)	0.3941	0.3193	0.2773	0.3031	0.3053	0.2856	0.2850
p ($E_{\text{col}}=0.5\text{eV}$)	0.3121	0.2773	0.2491	0.2477	0.2613	0.2412	0.2432

Figure 2 represents the calculated DCSs for $C(^3P) + CH(X^2\Pi)(v = 0, 2, 3, 4, 6, j = 0)$ at the collision energy $E_{\text{col}}=0.3$ eV. Clearly, the C_2 molecules scattered mainly in the forward-backward direction. Due to the effect of the potential well of PES, the long-life complex compounds are formed [27], which leads to the same chance between the forward

scattering and the backward scattering when the initial vibrational quantum number $v_{CH} = 0$. Overall, the reagent vibration excitation obviously enhances the strength of the forward scattering. One can see that the forward scattering achieves the maximum strength when the initial vibrational quantum number $v_{CH} = 3$. However, when the initial vibrational quantum number continues to increase, the effect of the potential well will reduce and the trend of forward scattering decreases. It must be said that the above phenomenon occurs for each of the four collision energies. We attribute this phenomenon to the property of the PES of the title reaction. It should be noted that the increase of the initial vibrational quantum number alters the reaction pathway. In order to gain a deep understanding of the reaction mechanism, we study the change of the reactive trajectories in **Figure 3**.

By randomly selecting reaction trajectory, we obtain the change graph of the internuclear distance of C_a-C_b , C_b-H and C_a-H as a function of propagation time for $v=0, 2, 4, 6$ at $E_{col}=0.3\text{eV}$. The **Figure 3 (a), (b), (c)** show that the attack atom C_a undergoes several collisions with the target molecule C_bH and then forms the complex compound C_aC_bH with a certain life before the final products C_aC_b come into being, which shows that the indirect reaction mechanism dominates the title reaction. Due to the long-term survival of the complex compound which allows the reaction to perform extensive rotations, it makes the product is mainly forward-backward scattering at $v_{CH} = 0$. It should be noted that the life of the complex compound will decrease and the collision times are reduced when the reagent vibrational quantum number increases. However, **Figure 3(d)** shows a direct reaction mechanism when the reagent vibrational quantum number $v=6$. In general, the above reaction is dominated by the indirect reaction mechanism, nonetheless, the direct reaction mechanism plays a role when the reagent vibrational quantum number increases to a certain degree.

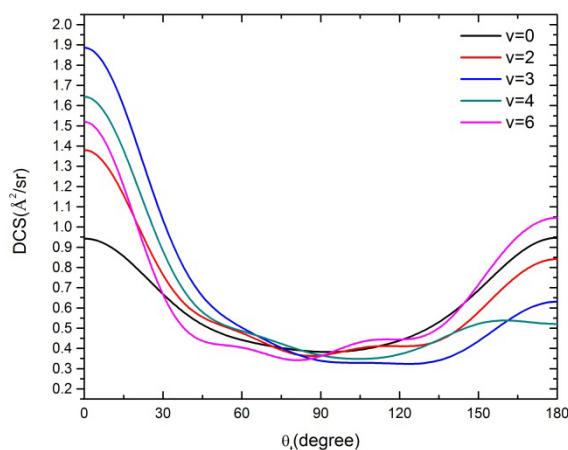


Figure 2: Differential cross section for $C(^3P) + CH(X^2\Pi)(v = 0, 2, 3, 4, 6, j = 0)$ at the collision energy $E_{col}=0.3\text{eV}$.

The $P(\theta_r)$ distribution of the product C_2 is shown in **Figure 4**, which describes the $\mathbf{k}-\mathbf{j}'$ correlation. One can see that the peaks of $P(\theta_r)$ distribution are at the angle $\theta_r = 90^\circ$ and are symmetric with respect to $\theta_r = 90^\circ$. This symmetric phenomenon implies that the product rotational angular momentum vector $\mathbf{j}'$ is strongly aligned along the direction at a right angle to the relative velocity direction $\mathbf{k}$ and this phenomenon has also been discovered in the reaction $H+LiH^+$ [27], H^++D_2 [28]. It is clearly observed that the peak of the $P(\theta_r)$ distributions becomes higher and narrower with the increasing of the reagent vibration excitation of the title reaction. In other words, the increase of the reagent vibrational energy will increase the anisotropic distribution of the product rotational angular momentum vector $\mathbf{j}'$.

To obtain a better understanding of the product rotational alignment distribution of C_2 , we calculate the product rotational alignment parameter $\langle P_2(\mathbf{j}' \cdot \mathbf{k}) \rangle$, which shows in **Figure 5**. $\langle P_2(\mathbf{j}' \cdot \mathbf{k}) \rangle$ can give us a quantitative description of the degree of the product rotational alignment. The value of $\langle P_2(\mathbf{j}' \cdot \mathbf{k}) \rangle$ changes from 1 to -0.5. The smaller the expectation value of $\langle P_2(\mathbf{j}' \cdot \mathbf{k}) \rangle$ is, the stronger the degree of the product rotational alignment is. It can be seen from **Figure 5** that the value of $\langle P_2(\mathbf{j}' \cdot \mathbf{k}) \rangle$ is on the decrease when the reagent vibrational quantum number increases. It means that the polarization degree of the product rotation has strengthened and the peak of the $P(\theta_r)$ distributions becomes higher. Therefore, the reagent vibrational excitation can increase the polarization degree of the product rotation and it confirms the correctness of the results from **Figure 4**.

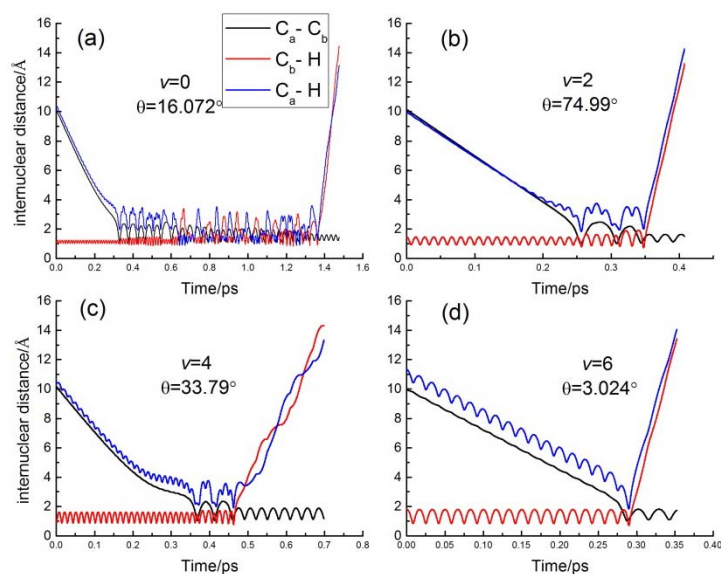


Figure 3: Change of internuclear distance of C_a-C_b , C_b-H and C_a-H as a function of propagation time for $v=0, 2, 4, 6$ at $E_{col}=0.3\text{eV}$.

Figure 6 shows the calculated $P(\phi_r)$ distribution for product C_2 at the reagent vibrational quantum number of 0, 2, 4, 6, respectively. In all case, the $P(\phi_r)$ distributions are asymmetric with respect to the $k-k'$ scattering plane, with the peaks appearing at $\phi_r = 90^\circ$ and 270° , which reveals that there is a strong polarization of the product angular momentum j' of the title reaction. It is clear from **Figure 6** that the peak at $\phi_r = 90^\circ$ is higher than that at $\phi_r = 270^\circ$. This behavior implies that the product rotational angular momentum vector j' is not only aligned, but also oriented along the positive y -axis. It also means that the products C_2 rotate along an anticlockwise direction. As a general view, the peak of $P(\phi_r)$ distribution increases and becomes a little narrower with the increase of the reagent vibrational quantum number, which reflects that the rotational polarization of the product is strengthened with the increase of the reagent vibrational quantum number. Therefore, the reagent vibrational excitation has a positive influence on the polarization of the product rotational angular momentum.

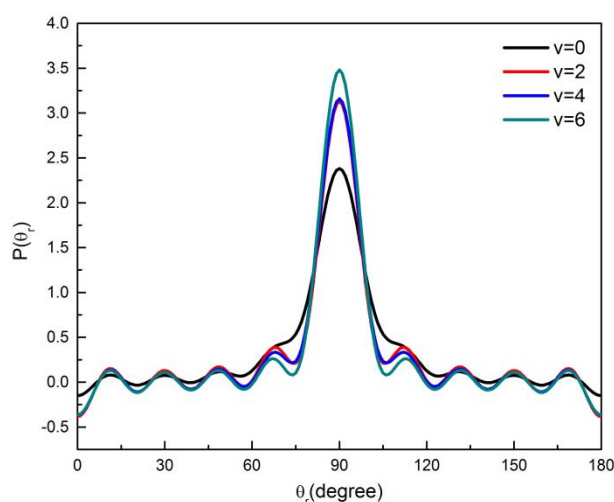


Figure 4: The distribution of $P(\theta_r)$ for $C(^3P) + CH(X^2I)(v = 0, 2, 4, 6, j = 0)$ at the collision energy $E_{col} = 0.3 \text{ eV}$.

In the present paper, we study the stereodynamics of $C(^3P) + CH(X^2I)(v = 0 - 6, j = 0) \rightarrow C_2 + H$ reaction using a QCT method on the $1^2A''$ PES constructed by Boggio-Pasqua et al. The Cross Sections and DCSs are obtained. The calculated DCSs show that the increase of the reagent vibrational quantum number could enhance the trend of the forward scattering of the title reaction. The plot of internuclear distance of C_a-C_b , C_b-H and C_a-H reveals that the direct mechanism can exist in this title reaction. The distributions of $P(\theta_r)$, and $P(\phi_r)$ in the different vibrational states of the reagent are also discussed. The $P(\theta_r)$ distribution shows that the alignment degree of the product angular momentum is strengthened with the increase of v_{CH} . The $P(\phi_r)$ distribution indicates that the product rotational angular momentum is not only aligned, but also oriented along the positive y -axis. The increase of

v_{CH} enhances the orientations degree of the product rotational angular momentum. It can be concluded that the stereodynamics of the title reaction is sensitively affected by the reagent vibrational excitation.

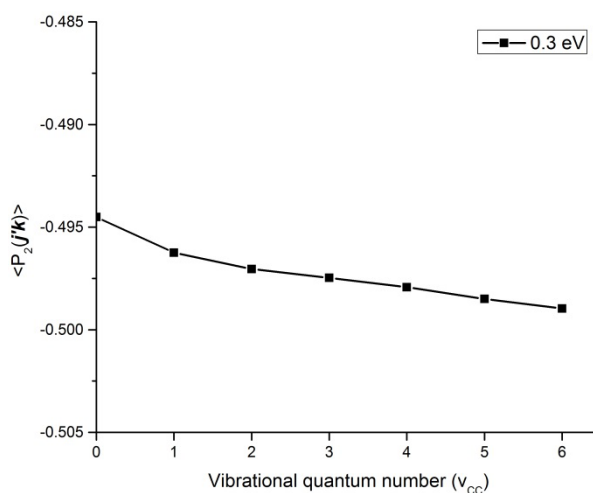


Figure 5: Rotational alignment parameter of the product $C_2 \langle P_2(j'k') \rangle$ for the reaction $C(^3P)+CH(X^2[1])$ ($v=0-6$, $j=0$) at the collision energy $E_{col}=0.3\text{eV}$.

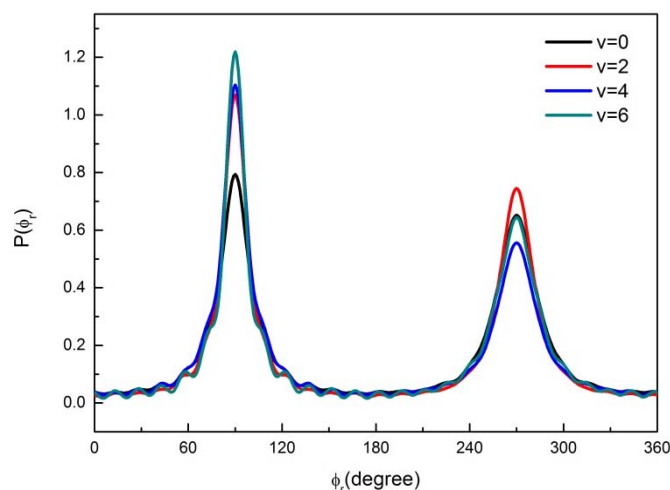


Figure 6: The dihedral angle distribution of $P(\phi_r)$ of the product C_2 for the reaction $C(^3P) + CH(X^2[1])$ ($v = 0, 2, 4, 6, j = 0$) at the collision energy $E_{col}=0.3\text{eV}$.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 11474142, 11074103) and Discipline Construction Fund of Ludong University. All

calculations were carried out in the Shuguang Super Computer Center (SSCC) of Ludong University. The authors also appreciate Professor Han for providing the QCT code of stereodynamics, as well as some precious advice.

References

- [1] D. Duflot, J.M. Robbe, and J.P. Flament. *Ab initio* potential energy surfaces for $C_2H \rightarrow C_2 + H$ photodissociation. J. Chem. Phys. 100 (1994) 1236-1246.
- [2] M. Boggio-Pasqua, A.I. Voronin, Ph. Halvick, J.-C. Rayez, Global analytical representations of the three lowest potential energy surfaces of C_2H , and rate constant calculations for the $C(^3P) + CH(^2\Pi)$ reaction. Phys. Chem. Chem. Phys. 2 (2000) 1693-1700.
- [3] B.Y. Tang, M.D. Chen, K.L. Han, J.Z.H. Zhang, Time-dependent quantum wave packet study of the $C + CH$ reaction. J. Chem. Phys. 115 (2001) 731-738.
- [4] Y.C. Hsu, J. Jr-Min. Lin, D. Papousek, J.-J. J. Sai, The low-lying bending vibrational levels of the $CCH(X^2\Sigma^+)$ radical studied by laser-induced fluorescence. J. Chem. Phys. 98 (1993) 6690-6696.
- [5] D.L. Lambert, Y. Sheffer, A.C. Danks, C. Arpigny, P. Magain, Astrophys. High-resolution spectroscopy of the C_2 Swan 0-0 band from Comet P/Halley. J. 353 (1990) 640-653.
- [6] W.M. Jackson, Y. Bao, R.S. Urdahl, Implications of C_2H photochemistry on the modeling of C_2 distributions in comets. J. Geophys. Res. 96 (1991) 17569-17572.
- [7] H. Suzuki, Synthesis of chain molecules in regions with partially ionized carbon. Astrophys. J. 272 (1983) 579-590.
- [8] S.L. Richardson, J.S. Francisco, A computational study of the reaction of C_2 with CH_4 . Mol. Phys. 83 (1994) 1041-1044.
- [9] D.C. Fang, X.Y. Fu, *Ab initio* studies on the IRC and rate constant of the reaction between acetylene and the hydrogen atom. Int. J. Quantum Chem. 49 (1994) 3-10.
- [10] J. Zhang, C.W. Riehn, M. Dilligan, C. Wittig, Propensities toward $C_2H(\tilde{A}^2\Pi)$ in acetylene photodissociation. J. Chem. Phys. 103 (1995) 6815-6818.
- [11] B.Y. Tang, M.D. Chen, K.L. Han, J.Z. H. Zhang, Time-dependent quantum dynamics study of the $C + CH$ reaction on the $2A'$ surface. J. Phys. Chem. A 105 (2001) 8629-8634.
- [12] B.Y. Tang, B.H. Yang, K.L. Han, R.Q. Zhang, J.Z.H. Zhang, Time-dependent quantum wave packet studies of the $F + HCl$ and $F + DCl$ reactions. J. Chem. Phys. 113 (2000) 10105-10113.
- [13] H.R. Yang, Z.Y. Liu, S.H. Sun, Quasi-classical study of stereo-dynamics for the reaction on the $1^2A'$ potential energy surface. J. Theor. Comput. Chem. 10 (2011) 75-91.
- [14] B.Y. Tang, B.H. Yang, K. L. Han, R. Q. Zhang, J. Z. H. Zhang, Time-dependent quantum wave packet studies of the $F + HCl$ and $F + DCl$ reactions. J. Chem. Phys. 113 (2000) 10105-10113.
- [15] H.R. Yang, Z.Y. Liu, S.H. Sun, Quasi-classical study of stereo-dynamics for the reaction on the $1^2A'$ potential energy surface. J. Theor. Comput. Chem. 10 (2011) 75-91.
- [16] P. Halvick, M. Boggio-Pasqua, L. Bonnet, Trajectory surface hopping study of the $C + CH$ reaction.

- Phys. Chem. Chem. Phys. 4 (2002) 2560-2567.
- [17] M. Boggio-Pasqua, A.I. Voronin, Ph. Halvick, Coupled *ab initio* potential energy surfaces for the two lowest $^2A'$ electronic states of the C_2H molecule. Mol. Phys. 98 (2000) 1925-1938.
- [18] T.X. Xie, Y. Shi, Reagent vibration effect on the stereodynamics for the $C+CD \rightarrow C_2+D$ Reaction. Chin. Phys. Lett. 28 (2011) 113101(1)-113101(4).
- [19] H.H. Zhang, C.J. Hu, Q. Wei, B. Zhang, Theoretical study of the dynamics of the reaction $C(^3P)+CH(X^2\Pi)$. Mol. Phys. 107 (2009) 2503-2509.
- [20] Z.Y. Liu, B.T. Hu, Theoretical study of stereo-dynamics for the reaction $C(^3P)+CH(X^2\Pi) \rightarrow C_2+H$ on the three lowest potential energy surfaces. J. Theor. Comput. Chem. 9 (2010) 1065-1073.
- [21] J. C. Wu, M.S. Wang, C. L. Yang, X. H. Li, X. Q. Chen, Theoretical study of the stereodynamics of the reaction $C(^3P)+CH(X^2\Pi)$ and its isotopic variants. Chin. Phys. Lett. 28 (2011) 063401(1)-063401(4).
- [22] K.L. Han, G.Z. He, N.Q. Lou, Effect of location of energy barrier on the product alignment of reaction $A+BC$, J. Chem. Phys. 105 (1996) 8699-8704.
- [23] M.L. Wang, K.L. Han, G. Z. He, Product rotational polarization in photo-initiated bimolecular reactions $A+BC$: Dependence on the character of the potential energy surface for different mass combinations. J. Phys. Chem. A. 102 (1998) 10204-10210.
- [24] T. G. Yang, J.C. Yuan, D.H. Cheng, M.D. Chen, Quasi-classical trajectory study of the effects of reactant ro-vibrational excitation on the $H+LiH^+ \rightarrow Li^++H_2$ Reaction. Commun. Comput. Chem. 1 (2013) 15-26.
- [26] M.D. Chen, B.Y. Tang, K.L. Han, N.Q. Lou, Quasi-classical trajectory study of the DCl/HCl product branching ratios for the $Cl+HD$ reaction on BW2 potential energy surface. Chem. Phys. Lett. 337 (2001) 349-354.
- [27] L.H. Duan, W.Q. Zhang, X.S. Xu, S.L. Cong, M.D. Chen, Theoretical studies of the stereodynamics for the reaction $H+LiH^+(v=0, j=0) \rightarrow Li^++H_2$. Mol. Phys. 107 (2009) 2579-2585.
- [28] C.H. Zhang, W.Q. Zhang, M.D. Chen, Theoretical studies of stereodynamics for the $H^++H_2(v=0-3, j=0) \rightarrow H_2+H^+$ reaction. J. Theor. Comput. Chem. 08 (2009) 403-415.