Product Polarization and State Distributions

of the Cl + HD Reaction

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Abstract　The dynamics of the Cl + HD reaction has been studied by means of quasiclassical trajectory calculations on both BW2 and G3 potential energy surfaces. The calculations show the product rotational alignment is sensitive to the potential energy surfaces and mass factors of reaction system. While the calculated product polarization on BW2 potential energy surface seems stronger than that on G3 potential energy surface for two products and the rotation of the DCl product is more strongly aligned in comparison with the HCl product in all cases. And also the calculations show the effect of the reagent rotational excitation on reactivity for both surfaces is significantly different. The initial rotational excitation has a positive influence on the reactivity for the Cl + HD reaction from calculations on the BW2 surface, while the effect of the reagent rotational excitation on reactivity is negative for G3 surface.

Key words　Quasiclassical trajectory calculation, Potential energy surface, Product rotational alignment

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1　Introduction

In order of full understanding the dynamics of the elementary reactions such as Cl + HD→HCl + D and Cl + HD→DCl + H, it is important to study not only its scalar properties, but also its vector properties. Only by understanding the scalar and vector properties together can the fullest picture of the scattering dynamics emerge. The most familiar vector correlation is that between the reagent and product relative velocity (**K**, **K'**) with is characterized by the differential cross section $\frac{d\sigma}{d\omega_t}$. The vectors **K**, **K'** and **J'** (the product rotational angular momentum) are also interesting; the angular distribution describing the relative orientation of these vectors in space may be termed the **K-K'-J'** distribution and the correlations which characterize it, double and triple vector correlations. Vector properties, such as velocities and angular momenta, possess not only magnitudes that can be directly related to transnational and rotational energies, but also well-defined directions. Clearly, one of the most important things is the determination of the product rotational alignment and orientation about the regent's relative velocity vector. Experimental and theoretical interest in vector correlation in the reaction processes A + BC → AB + C has increased significantly in recent decades[1-14]. With the development of experimental and theoretical studies for three-atom systems, it is becoming increasingly clear that product rotational polarization can provide detailed mechanistic information. Recently, many groups turn their attention to the complex-forming four-atom systems[15-20]. Such systems are more interesting because angular momentum conservation in four-atom systems are unlikely to impose such severe constraints on product rotation as in three-atom reactions. Furthermore, the rotation of the reactive in-

termediate prior to dissociation will lead to some loss or smearing-out of polarization.

During the development of gas-phase reaction dynamics the reaction Cl + H$_2$ and its isotopic variants have played a key role. Due to its importance in atmospheric chemistry and for photochemical air pollution, the reaction of chlorine atoms with molecular hydrogen has received considerable attention both experimentally and theoretically[2][35]. The reaction Cl + H$_2$ and its isotopic variants have been a prototypical three-atom reaction system in the field of molecular reaction dynamics and have served as test cases for bimolecular reaction rate theory[36], particularly transition state theory[37] and the theory of isotope effects[38]. The isotope effects in reaction dynamics are kinetically interesting for they provide different dynamic view on the same potential energy surface (PES).

On the experimental side, the infrared frequency-modulation measurements of absolute rate constants for the Cl + HD reaction between 295 K and 700 K have been reported by Taatjes[32]. Alagia et al. have measured angular distributions and time-of-flight spectra for the reactions Cl + H$_2$ and Cl + D$_2$ using high-resolution crossed molecular beam experiments[34]. Kandel et al. report the vibrationally state-resolved differential cross-sections and product rotational distributions for the Cl + HD reaction using a photoinitiated reaction technique[35]. In addition, the effect of HD reagent rotational alignment in this reaction has also been investigated[15]. On the theoretical side, several potential energy surfaces for the ClH$_2$ system have been constructed and many dynamical calculations on these surfaces have been performed. The first potential energy surface (PES) for this system was suggested by Eyring and co-workers in 1936[37]. A refined potential energy surface named G3 was introduced by Truhlar and co-workers[29]. The G3 PES was based on the GQQ PES of Schwenker et al.[24], which was based on the GSW surface and some new ab initio data. The G3 PES has been successful in reproducing rate constants[39] and molecular beam measurements[28] from QM[28,29] and QCT[28,40] dynamical calculations.

The QM and QCT dynamical calculations based on the G3 PES are in good agreement with earlier experiment, so the G3 potential energy surface is regard as the most accurate surface currently available for the HHCl system. However, recent molecular beam experiments of Liu for the reactions Cl + HD and Cl + H$_2$ are in strong disagreement with theoretical calculations on G3 potential energy surface[41][43]. The crossed molecular beam experiments on the reaction Cl + HD revealed a strong preference for the production of DCl[42], while the QM calculations on the G3 potential energy surface predict the HCl and DCl products to be produced almost equally. Liu and co-workers have measured the effects of H$_2$ rotational states and Cl spin-orbit states on the Cl + H$_2$($v = 0$) excitation function and additionally report that the vast majority of HCl products are back scattered[41,43]. The effect of reagent rotation should be positive for the Cl + H$_2$ reaction, but the QM and QCT calculations on the G3 PES show that the effect of reagent rotation is negative. So Bian et al. presented a new global three-dimensional PES[44] named BW2 for Cl + H$_2$ system which has been computed using the most accurate electronic structure methods and basis sets presently available. In contrast to the G3 PES, the exact QM reactive scattering calculations for this system on the BW2 PES predicted the large DCl/HCl branching ratios at low collision energies correctly and in better agreement with the recent crossed molecule beam experiment measurement[42].

In our previous papers, time-dependent (TD) quantum wave packet dynamics studies have been performed on both G3 and BW2 PESs for the reaction Cl + HD and its isotopic variants[45][47]. The significant differences in the energy dependence of the reaction probabilities and integral reaction sections on the two surfaces have been found. The dynamics of the Cl + HD reaction has also been studied using quasiclassical trajectory calculations on BW2 potential energy surface[48]. The DCl/HCl product branching ratios calculated quasiclassically on this surface predict a clear preference to the production of DCl over HCl, which is in reasonable agreement with experimental result and some other theoretical results as well. While these first calculations have been pointing to a different behaviour

of the two surfaces, a test of the new surface against the other available dynamical observables has still to be performed. So, in this paper we focus our attention on the calculations of product rotational alignment for the Cl + HD reaction in order to learn more about the potential energy surface and more dynamical information from vector properties than from scalar properties.

2　Theory

2.1　Rotational alignment

During a reactive encounter, the total angular momentum is conserved

$$\mathbf{J} + \mathbf{L} = \mathbf{J}' + \mathbf{L}'$$

where $\mathbf{L}$ and $\mathbf{L}'$ are the reagent and product orbital momenta, respectively. When the reagent angular momentum $\mathbf{J}$ is small (as is common), the product rotation can only result from $\mathbf{L}$. The distribution of the angular momentum $\mathbf{J}'$ of the product molecule is described by a function $f(\theta)$, where θ is the angle between $\mathbf{J}'$ and the relative velocity vector $\mathbf{K}$. $f(\theta)$ can be represented by Legendre polynomial moments[1,2].

$$f(\theta) = \sum a_n P_n(\cos\theta)$$

$n = 2$ indicates the product rotational alignment,

$$\langle P_2(\mathbf{J}' \cdot \mathbf{K}) \rangle = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle$$

where P_2 is the second Legendre moment, and the brackets indicate an average over the distribution of $\mathbf{J}'$ about $\mathbf{K}$. At present, we only calculate the rotational alignment parameters of the product since it has solely been measured in most experiments until now.

2.2　Quasiclassical trajectory calculations

In this paper two different potential energy surfaces have been employed: one from G3[29], and the other from BW2[44]. The comparisons of two surfaces have been extensively studied in the previous work[44-48].

The general method for the calculation of quasiclassical trajectories is the same as the one used previously[11-14,48,49], the classical Hamilton's equations are integrated numerically for motion in three dimensions. The state-resolved differential cross sections are calculated by the method of moments expansion in Legendre polynomials[50]. Now, we have carried out the calcula-

tions of the reaction cross sections with the variation of collision energy for the reaction Cl + HD($v = 0, j = 0, 1$) on both G3 and BW2 PESs. The product final rotational state distributions and the product angular distributions are performed at $E_c = 23.4$, 27.2, 33.4 kJ/mol for this system. Additionally, we calculate the rotational alignment parameters of the HCl and DCl products for the Cl + HD ($v = 0$, $j = 0$) reaction on two surfaces. Batches of 10^5 trajectories are run for each initial condition, and the integration step size in the trajectories is chosen to be 0.1fs, which guarantees the conservation of the total energy and angular momentum.

3　Results and discussion

Fig. 1 presents some notable differences in the integral cross sections calculated on the BW2 and G3 surfaces. First, in contrast to the prediction on G3 PES, the QCT calculations on BW2 PES shown in bottom panel reveala dramatic preference for producing DCl for the Cl + HD→HCl + D and Cl + HD→DCl + H reactions. These phenomena are in agreement with the experimental results[42] and have attracted us to investigate in the previous work[48]. Second, the absolute cross sections obtained on BW2 PES are smaller than their counterparts calculated on G3 PES, particularly for the HCl product. The quasiclassical results agree well with the results calculated using time-dependent quantum wave packet theory for the Cl + HD reaction[47]. And also the calculated results indicate the effect of the van der Waals forces is more pronounced for producing the HCl product. As the center of the mass of HD is closer to the D atom, and thus, the H atom encounters the van der Waals forces at a larger HD-to-Cl separation. Third, the top panel in Fig. 1 shows the reagent rotational excitation has a negative influence on reactivity for the Cl + HD reaction for both DCl and HCl products from calculations on the G3 surface. However, as shown in bottom panel, the effect of rotational excitation from the calculations on BW2 surface is positive. In our earlier work, the time-dependent quantum wave packet method has been employed to calculate the total integral cross sections for this reaction[47]. While the calculations based on BW2 surface also show the effect
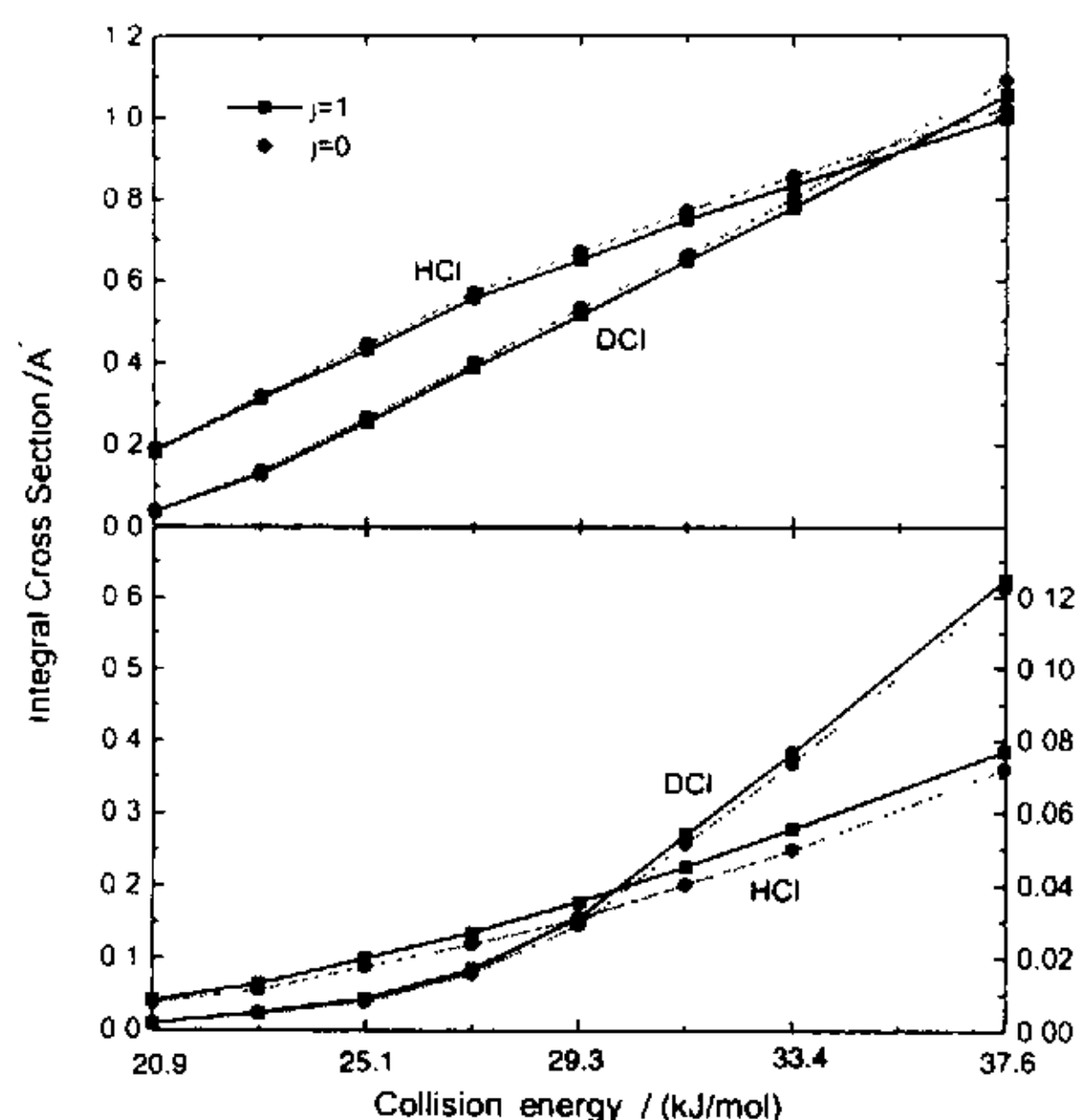
Fig. 1　Integral cross section as functions of collision energy
for the Cl + HD ($v = 0$, $j = 0,1$) reaction

The top panel shows the calculations on the G3 PES and
the bottom panel shows the calculations on the BW2 PES.
The right Y-axis on bottom panel indicates the calculated
results for the HCl product.

Fig. 2　Integral cross section as a function of final rotational state of the
HCl and DCl products from the Cl + HD ($v = 0$, $j = 0$) reaction
G3 and BW2 indicate the results calculated on the G3
and BW2 potential energy surfaces, respectively.
The right Y-axis indicates the calculations on G3 PES.

of reagent rotational excitation on reactivity is positive.
For the calculations on BW2 PES, it reveals the effect
of rotational excitation is positive for the Cl + H$_2$ reaction, which are in nice agreement with the recent molecular beam experiments of Lee et al. [41]. Therefore, the new BW2 PES predicts the right effect of the initial rotational excitation for the reaction Cl + HD and its isotopic reactions.

Fig. 2 depicts the HCl and DCl product rotational state distributions calculated on G3 and BW2 PESs for the Cl + HD ($v = 0$, $j = 0$) reaction at collision energies $E_c = 23.4$, 27.2, 33.4 kJ/mol. The calculations show once more the BW2 surface is less reactive than the G3 surface and the effect of BW2 on reactive is more significant for the Cl + HD→HCl + D channel. However, the final rotational state distributions calculated on BW2 surface are similar to those on G3 surface for both HCl product and DCl product except that the final rotational states on G3 are little hotter than those predicted on BW2 surface. The corresponding differential cross sections (DCS) of the DCl and HCl products for the Cl
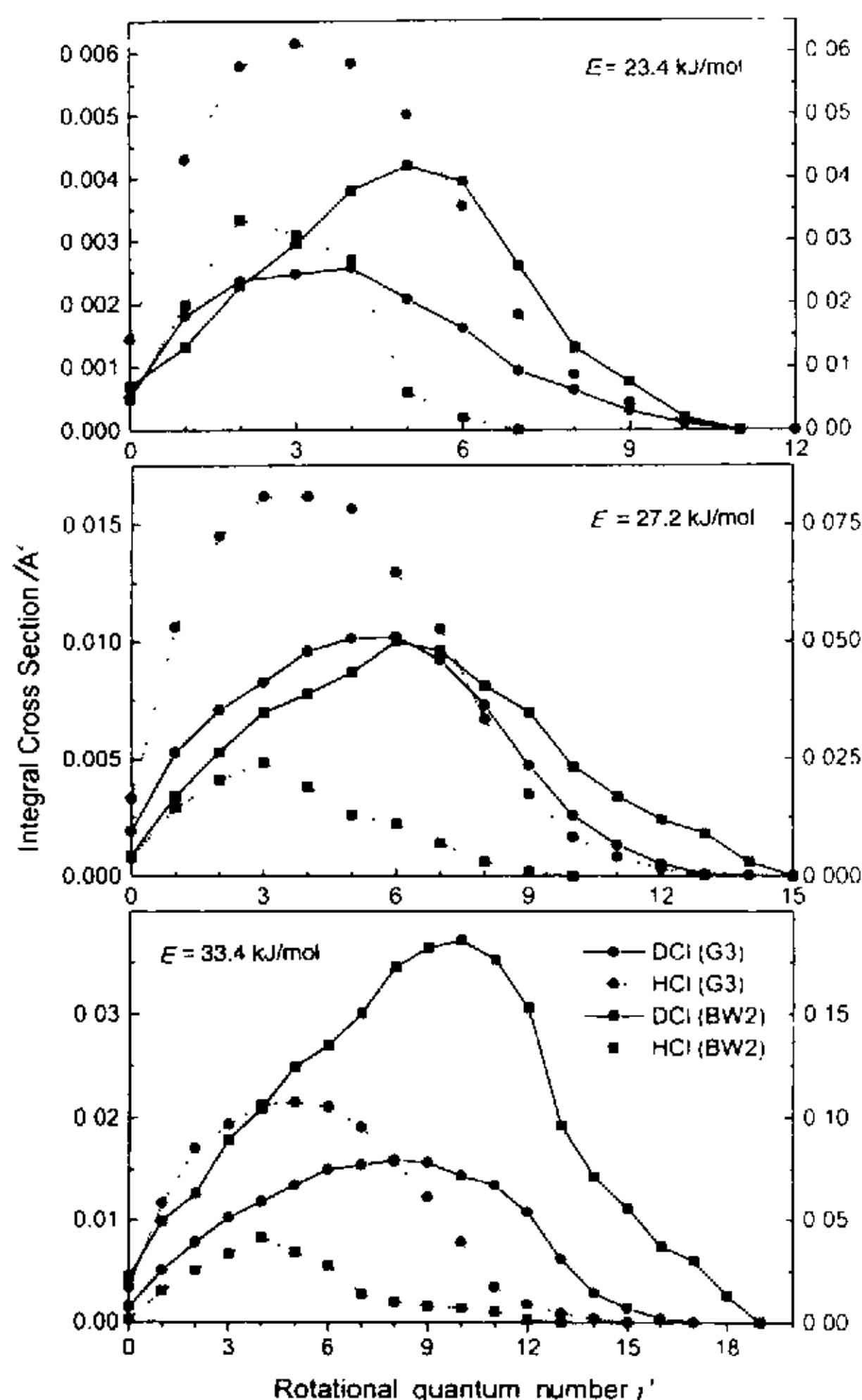
+ HD ($v = 0$, $j = 0$) reactions calculated on both G3 and BW2 PESs at the same collision energies are presented in Fig. 3. For the calculations on both PESs, it predicts backward scattered molecular product including larger sideways contributions as the collision energy increases. Although the HCl product shows a preference for sideways scattering on BW2 surface, the angular distributions of DCl product computed on BW2 are almost similar to those calculated on G3 surface. The agreement between DCSs and product rotational distributions calculated on both surfaces probably arise from the similar characters of two surfaces, which have collinear transition states. While the barrier height of the BW2
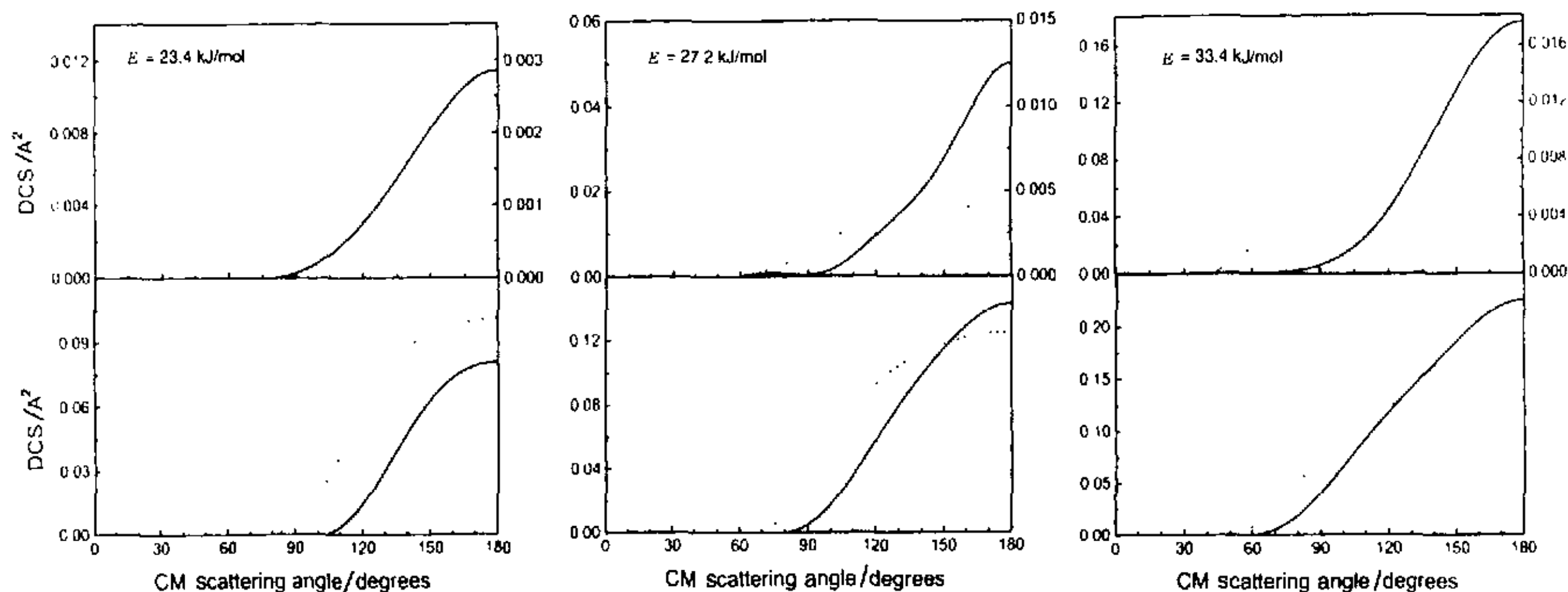
Fig. 3　Differential cross sections for the Cl + HD ($v = 0$, $j = 0$) reaction

The top three panels show the results calculated on the BW2 PES and the right Y-axis indicates the
calculations for the HCl product. The bottom three panels show the results calculated on the G3 PES.

surface (31. 81 kJ/mol) is quite close to that of the G3 surface (32. 94 kJ/mol). The harmonic vibrational frequencies of the bending and stretching coordinates at the transition state are also pretty similar.

As to investigate the isotope effect and the effect of different surfaces on vector correlation, the product rotational alignment parameters $\langle P_2(\mathbf{J}' \cdot \mathbf{K}) \rangle$ for the Cl + HD reaction on BW2 and G3 PESs have been calculated and the results are shown in Fig. 4 and Fig. 5. It is very obvious that the product rotational angular momentum for both the DCl and HCl products is aligned either on BW2 PES or on G3 PES, and the variety of the product rotational alignment with the change

of j' is also similar on both PESs. The $\langle P_2(\mathbf{J}' \cdot \mathbf{K}) \rangle$ values for DCl and HCl products calculated on both surfaces are increasing with the increases of the collision energies and are decreasing as the increases of the final rotational quantum number j'. Generally, the higher the collision energies are, the stronger the rotational alignment of the products will be. However, the $\langle P_2(\mathbf{J}' \cdot \mathbf{K}) \rangle$ values calculated on both BW2 and G3 PESs for the Cl + HD reaction increase as the collision energy increases in present work. The reason is that the collision energies studied in present work are close to the energy threshold. This phenomenon agrees with the calculations for HLL (H, heavy; L, light) mass
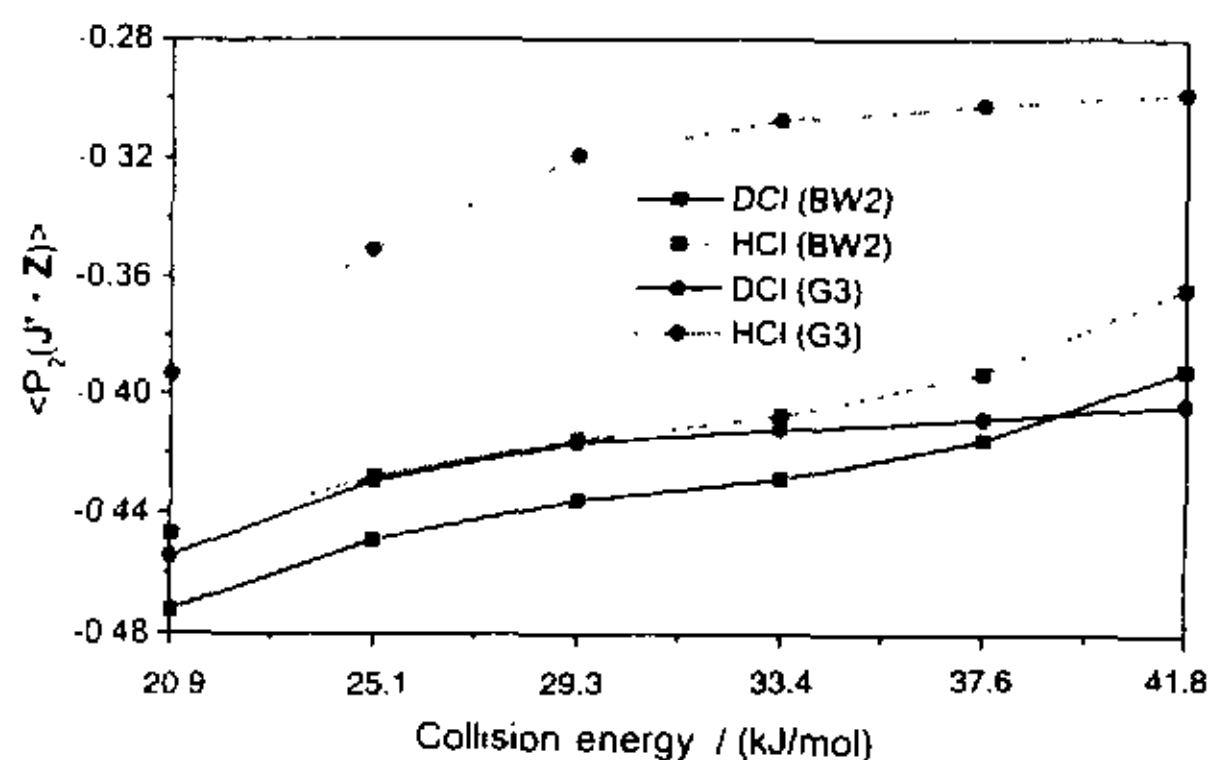

Fig. 4　Product rotational alignment parameters as functions of
collision energy for the Cl + HD ($v = 0$, $j = 0$) reaction
G3 and BW2 indicate the calculations on the G3
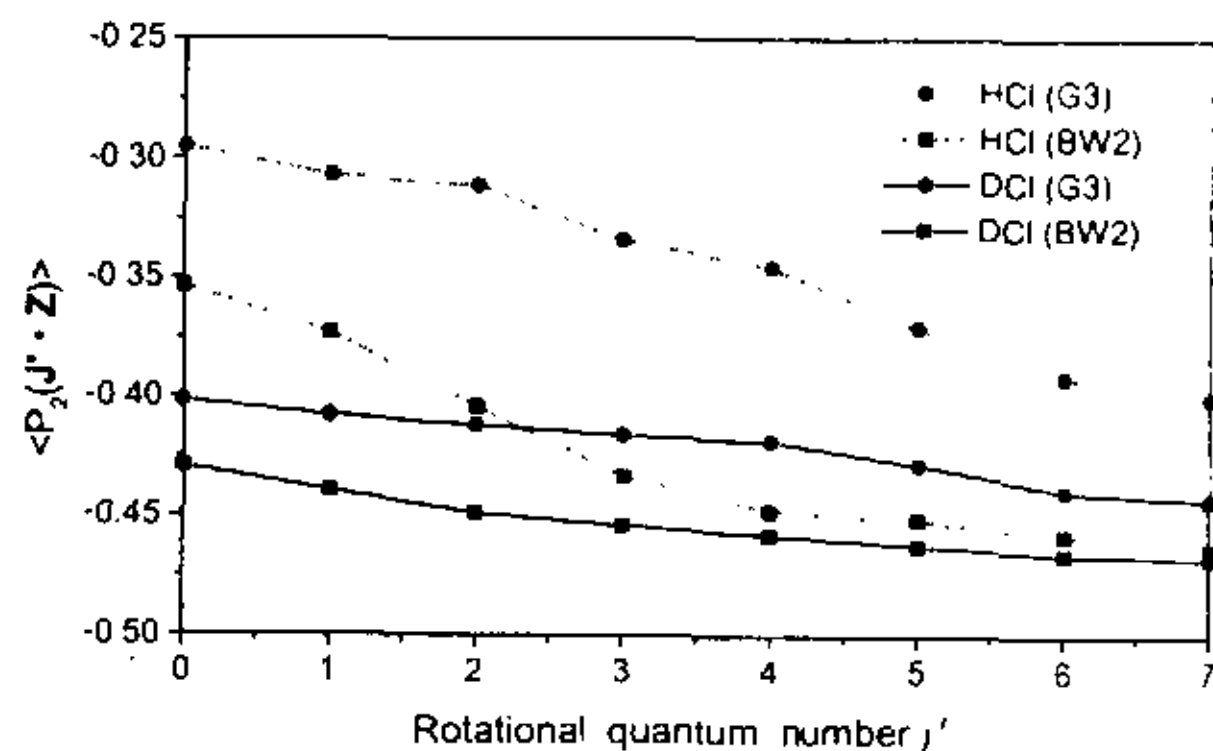and BW2 potential energy surfaces, respectively

Fig. 5　Product rotational alignment parameters as functions of final
rotational state for the Cl + HD ($v = 0$, $j = 0$) reaction
G3 and BW2 indicate the calculations on the G3
and BW2 potential energy surfaces, respectively

combination reaction on an attractive potential energy surface reported in Ref. [51]. In that paper we studied the dependence of the product rotational alignment on collision energies for HHL, HHH, HLL and LHL mass combination reactions on attractive and repulsive potential surfaces[51]. Calculations on BW2 PES show the product polarization is stronger than that calculated on G3 PES. Maybe the difference attributes to the saddle point of the BW2 surface is located earlier in the entrance channel than that of the G3 surface. The repulsive energy provides a distribution of the rotational angular momentum vector of the product which is less anisotropic. So the product rotation calculated on BW2 PES be strongly aligned even at very low collision energies due to that BW2 is so attractive than G3. It is well known that the well in the PES can affect the rotational alignment of the products, because it may lead to "loss of" memory of angular momentum alignment in that the separation of the products will take various direction in space. The most outstanding difference between BW2 and G3 PESs is the BW2 surface has long-range van der Waals minima in both the entrance and exit channels. However, the degree of the polarization for the HCl and DCl products calculated on the BW2 PES is stronger than that on the G3 PES. So, to draw a conclusion that probably the product rotational alignment is mainly controlled by the characters of transition state regions, and the effect of van der Waals force on product polarization is quite weak.

The calculations of product rotational alignment for the Cl + HD reaction show the notable isotope effects. Fig. 4 and Fig. 5 depict the rotation of the DCl product is so strongly aligned in comparison with the HCl product in all cases. Our previous work[51-53] has explored the product polarization for the H + H'L mass combinations reaction in detail and found that the distribution of the product angular momentum vectors is quite sensitive to the mass factors. For this reaction,

as the mass factor $\cos^2 \beta \approx \dfrac{m_H m_L}{(m_H + m_{H'})(m_{H'} + m_L)}$ approaches zero, the product rotational angular momentum vector is strongly aligned with respect to the relative velocity direction. The increase in mass factor

$\cos^2\beta$ will reduce the anisotropic distribution of $\mathbf{J}'$ by about $\mathbf{K}$. The effect of mass factor on product rotational alignment is also notable for the Cl + HD reaction. For the Cl + HD → HCl + D channel the mass factor is larger than that for the Cl + HD → DCl + H channel with the same PES. So the large mass factor lead to the $\langle P_2(\mathbf{J}' \cdot \mathbf{K}) \rangle$ values of HCl product become less negative and the product rotational angular momenta $\mathbf{J}'$ tend towards a less anisotropic distribution with respect to the direction of the vector $\mathbf{V}_{rel}$. In contrast to the HCl product, the rotation of the DCl product is thought of being strongly aligned in all cases.

4 Conclusions

The above comparison of excitation functions calculated on both PESs for the Cl + HD ($v = 0$, $j = 0$, 1) reactions has shown the different features between BW2 and G3 PESs lead to some different dynamical phenomena. In contrast to the prediction on G3 PES, the QCT calculations on BW2 PES reveale a dramatic preference for producing DCl for the Cl + HD→HCl + D and Cl + HD→DCl + H reactions. The BW2 surface is less reactive than G3 surface due to the influence of van der Waals well in the entrance valley of the BW2 surface. The effect of rotational excitation on reactivity from the calculations on BW2 surface is positive, while the reagent rotational excitation has a negative influence on reactivity for G3 surface.

The calculations on both BW2 and G3 PESs show the product rotational angular momentum is aligned and the variation trend of product rotational alignment effect with the change of the collision energies and the final rotational quantum number j' is similar. The predicted final rotational state distributions and angular distributions on both surfaces are also so similar. Comparison of the BW2 potential energy surface and the G3 surface, the transition state regions are broadly similar. Therefore, the similarity of the final rotational state distributions, angular distributions and the product polarization calculated on both surfaces imply that these dynamics properties are mainly controlled by the characters of transition state regions in PES. The calculations of the product rotational alignment show that the vector

correlation in Cl + HD reaction is sensitive to mass factors and the potential energy surfaces of reaction system. The rotational alignment effects of HCl product are smaller than DCl product in all cases as the mass factor is larger for the Cl + HD→HCl + D channel. The minor differences of the properties in transition state regions between BW2 and G3 surfaces result in a significant distinctness for the product polarization. Comparing with the scalar characters, the vector correlation in reaction is more sensitive to the potential energy surface, especially for the properties in the transition state regions. We look forward to the completion of experimental studies of product rotational alignment effect on the Cl + HD reaction so that a higher resolution comparison of theory and experiment can be implemented.

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Cl + HD 反应产物的极化与态分布

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摘 要： 利用准经典轨线理论，在 BW2 和 G3 两个势能面上，研究了 Cl + HD 反应的动力学. 计算结果表明，产物的转动取向对势能面及反应体系的质量因子非常敏感. 在 BW2 势能面上，计算的两个产物的转动取向强于在 G3 势能面上计算的结果，而无论是在 BW2 势能面上还是在 G3 势能面上，DCl 产物的取向都强于 HCl 产物的取向. 计算结果还表明，在不同的势能面上反应物的转动激发对反应的影响有着显著的不同. 在 BW2 势能面上，反应物的初始转动激发有利于 Cl + HD 反应的进行；而在 G3 势能面上，反应物的初始转动激发消弱了反应的反应性.

关键词： 准经典轨线理论；势能面；产物的转动取向

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