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Quantum stereodynamics study for the reaction F + HD*

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This paper studies the quantum stereodynamics of the F + HD($v = 0, j = 0$) → HD + F/HF + D reaction at the collision energies of 0.52 and 0.87 kcal/mol. The quantum scattering calculations, based on Stark-Werner potential energy surfaces, show that the differential cross sections for the HF($v' = 2$) + D and DF($v' = 3$) + H channels are consistent with the recent theoretical results. Furthermore, the product rotational angular momentum orientation and alignment have been determined for some selected rovibrational states of the HF + D and DF + H channels.

Keywords: stereodynamics, differential cross section, polarization parameters
PACC: 3400, 3520B

1. Introduction

The stereodynamics of chemical reaction has attracted enormous attention in the last few years, most attention deals with vector properties that characterize reactive molecular collisions.[1−3] Vector properties, such as velocities and angular momentums, not only possess magnitudes that are directly related to translational and rotational energies, but also well defined directions.[3] In contraposition to scalar properties such as integral cross sections, energy requirements for reaction, product energy disposal, population of quantum states, reaction probabilities, etc., the importance of the vector properties lies in the fact that chemical reactions were intrinsically anisotropic. This anisotropy was induced by the interatomic interactions and connections of reagents and products that are governed by the potential energy surface (PES).[3,4] It was expected that the understanding of the correlations among the different vectors involved in a reactive system will offer clues about the topology of the PES, and deepen the understanding of collision mechanisms.[1−4]

Using polarized lasers for both initiations and the probing stage of photon-initiated reaction sequence provided a means of probing product state-resolved rotational polarization as a function of center-of-mass scattering angle.[5,6] As far as the theory is concerned, a substantial progress towards the establishment of unified means to describe the vector correlations has been made in the past few years. Recently, quantum mechanical (QM)[7] formulations have been developed to extract those observations to be susceptible which can be determined by experiment from the scattering matrix. Another important step was the concept of polarization-dependent differential cross section (PDDCS) introduced by Shafer-Ray *et al.*[8] These quantities are a natural generalization of the usual differential cross section (DCSs). They can be determined both through experiment[9,10] and theory, and in the last case with either quasiclassical[4,10−14] or quantum methods.[13,15]

The F + HD reaction has been served as an archetypal system for the study of chemical reaction dynamics and a series of successive improvements in experimental and theoretical methods have given a detailed description about it.[16−27] However, most of the attention has been focused on the reactive resonance of this reaction, not the aspect of stereodynamics, for example, the time delay of F + HD → HF + D and F + H_2 → HF + H reactions were computed explicitly by Chao and Skodje.[19]

It has been generally believed that resonances

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should be sought in the differential cross section for collision experiments, since impact parameter averaging is expected to smear out resonance features in the total reactive cross section. However, in a crossed-molecular experiment of Liu and co-workers,[16−18] the total reactive cross sections for the HF + D and DF + H channels were obtained in the collision energy range of 0.2–5 kcal/mol and the clear evidence for a reactive resonance is found in the integral cross section for the reactive channels F + HD and HF + D at collision energy near 0.5 kcal/mol, while in the differential cross section it is manifested as sharply varying forward-backward peaks in the product distribution. Theoretical scattering calculations reproduce the shape of the resonance feature.[16−18] A detailed analysis of quantum dynamics using the spectral quantization method reveals that, at collision energies below 1 kcal/mol, the reaction was found to proceed almost exclusively through resonant tunneling with very little contribution from direct reaction over the barrier.[16−18] The experimental and theoretical studies of the F + HD reaction, to the best of our knowledge, are only limited to scalar properties such as the product state distributions, or to the simplest and most common vectorial property, which is the differential cross section (DCS). Other vectorial properties, such as product rotational angular momentum alignment, have not been studied for this system both experimentally and theoretically. In fact, it is of interest to study the stereodynamics of F + HD, particularly at the collision energy where the reactive resonance takes place. This article presents a quantum-mechanical (QM) study of the stereodynamics of the F + HD ($\upsilon = 0, j = 0$) reaction on the Stark–Werner potential energy surface, in which Chen *et al* have employed a recently developed unified quantum description of the stereodynamics of elementary atom-diatom reactions.[13]

2. Theory

2.1. Quantum Density Matrices

The QM PDDCSs and polarization parameters (PPs) have been obtained by using the same procedures and conventions as those in Refs.[15] and [28]. For the definite j states, the elements of the quantum θ-dependent rotational-space density matrix $\rho(\cos\theta)$ can be written in terms of adjoint multipole operators or Clebsch–Gordan coefficients as

$$\langle j'm_1'|\,\rho(\cos\theta)\,|j'm_2'\rangle = \frac{1}{2j'+1}\sum_{k=0}^{2j'}\sum_{q=-k}^{k}(2k+1)\left(\frac{2\pi}{\sigma}\frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega}\right)\langle j'm_1', kq|j'm_2'\rangle\,. \tag{1}$$

Using the orthogonality of the Clebsch–Gordan coefficients to invert this equation, we get the following expression for the θ-dependent expansion coefficients (quantum PDDCSs):

$$\frac{2\pi}{\sigma}\frac{\mathrm{d}\sigma_{kq'}}{\mathrm{d}\omega} = \frac{1}{p}\sum c(J_1,m,m_1',\theta)[c(J_2,m,m_2',\theta)]^*(-1)^{k+q'}\,\langle jm_1', kq'|jm_2'\rangle\,, \tag{2}$$

where

$$c(J_2,m,m_2',\theta) = (2J+1)d^J_{mm'}S_{v'j'm',vjm}, \tag{3}$$

in which $d^J(\theta)$ is the reduced Wigner rotation matrix and the normalized factor p is given by

$$p = \sum_{j,mm'}(2J+1)\,|S_{v'j'm',vjm}|^2. \tag{4}$$

Once the PDDCSs in the $x'y'z'$ frame (z' parallel to $\boldsymbol{k}'$, y' parallel to $\boldsymbol{k}\times\boldsymbol{k}'$) are calculated by Eq.(2), they are rotated to the xyz frame (z parallel to $\boldsymbol{k}$, y parallel to $\boldsymbol{k}\times\boldsymbol{k}'$) with

$$\frac{2\pi}{\sigma}\frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega} = \sum_{q'}d^k_{q'q}\frac{2\pi}{\sigma}\frac{\mathrm{d}\sigma_{kq'}}{\mathrm{d}\omega}. \tag{5}$$

The renormalized PDDCSs are defined as

$$\frac{\mathrm{d}\sigma_{kq}/\mathrm{d}\omega}{\mathrm{d}\sigma_{00}/\mathrm{d}\omega} = \sum_{m_1'm_2'}\langle j'm_1'|\,\rho(\cos\theta)\,|j'm_2'\rangle\,\langle j'm_1', kq|j'm_2'\rangle\,. \tag{6}$$

Integration of Eq.(5) over the scattering angle θ leads

to polarization parameter

$$a_q^{(k)} = \int_{-1}^{1} \frac{2\pi}{\sigma} \frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega} \mathrm{d}\cos\theta. \quad (7)$$

The polarization parameters give the absolute contributions of the multipolar matrices corresponding to k and q of the density matrix $\rho(\cos\theta)$, integrated over all scattering angles. The expansion coefficients $a_q^{(k)}$ have the same physical meaning of the classical case. The real polarization parameters are given by

$$a_{q+}^{\{k\}} = \frac{1}{\sqrt{2}} \left[(-1)^q a_q^{(k)} + a_{-q}^{(k)} \right], \quad 1 \le q \le k, \quad (8)$$

$$a_{q-}^{\{k\}} = \frac{1}{\mathrm{i}\sqrt{2}} \left[(-1)^q a_q^{(k)} - a_{-q}^{(k)} \right], \quad 1 \le q \le k, \quad (9)$$

$$a_0^{\{k\}} = a_0^{(k)}. \quad (10)$$

Similar formulae hold for the PDDCSs.

2.2. Calculation of quantum stereodynamical parameters

The QM scattering calculations have been carried out by using the CCP6 quantum reactive scattering program based on a coupled-channel hyperspherical coordinate method, which has been used in previous studies on the reaction dynamics of the H + D_2,[23−25] F + H_2,[26] F + HD[12,13] as well as Cl + H_2/HD[22] reactions. Here the calculations of the F + HD($v = 0, j = 0$) are performed on the SW surface at collision energies of $E_{\mathrm{col}} = 0.52$ and 0.87 kcal/mol.

The differential cross sections and the polarization parameters are calculated with the expressions previously used by Miranda and co-workers.[28] The physical and "directional" meanings of real expansion of the polarization parameters and $\dfrac{\mathrm{d}\sigma_{kq}/\mathrm{d}\omega}{\mathrm{d}\sigma_{00}/\mathrm{d}\omega}$ of ranks 1 and 2 according to the definitions have been given in Ref.[28].

3. Results and discussion

In order to check that the calculations are converged, we have computed the differential cross sections for the title reaction. The differential cross sections for HF($v' = 2, j' = 1, 10$) + D channel are presented in Fig.1. Clearly, it is backward scattering at collision energy of 0.52 kcal/mol but it shifts to sideways and forward distributed at $E_{\mathrm{col}} = 0.87$ kcal/mol. Also a backward angular distribution can be seen in Figure 2 for the DF($v' = 2, 3, j' = 1, 12$) + H channel at $E_{\mathrm{col}} = 0.87$ kcal/mol. Those results have the same

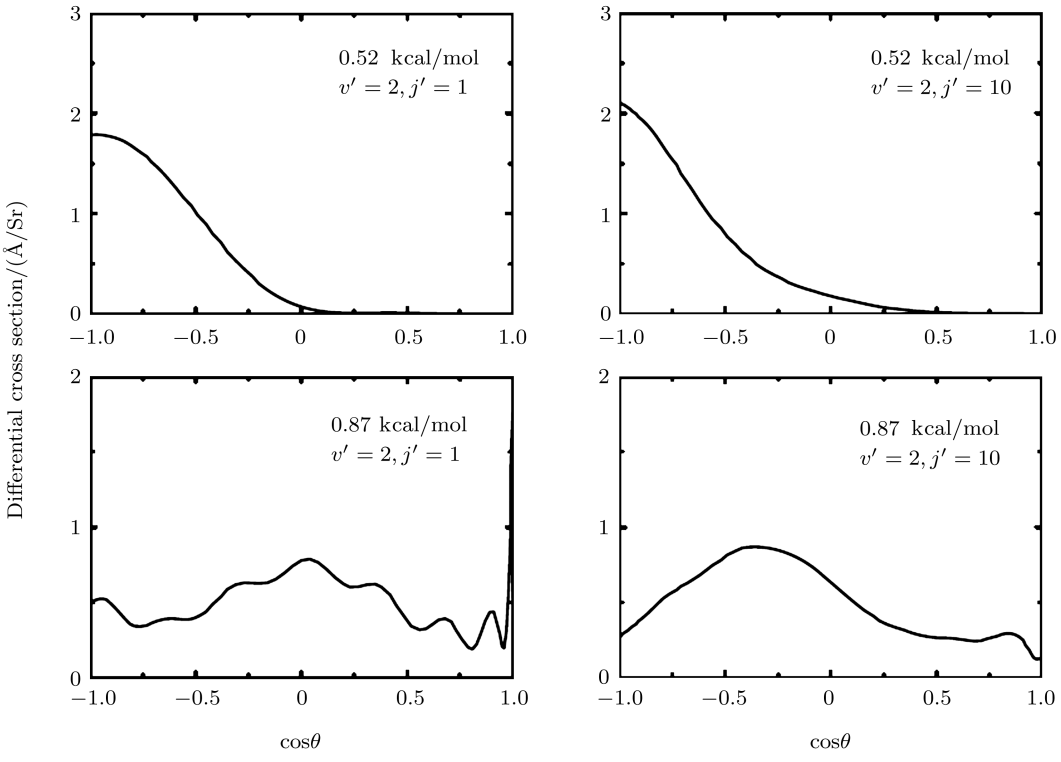


Fig.1. The differential cross section for D + HF($v' = 2$, $j' = 1, 10$) channel at collision energies of 0.52 kcal/mol and 0.87 kcal/mol (1 Å = 0.1 nm).

variation trend with the collision energy, and are in good agreement with the results of Ref.[17]. This confirms the previous study of this isotope channel, which is the expected behavior for a direct abstraction reaction with a rebound mechanism when it is viewed within the classical framework.

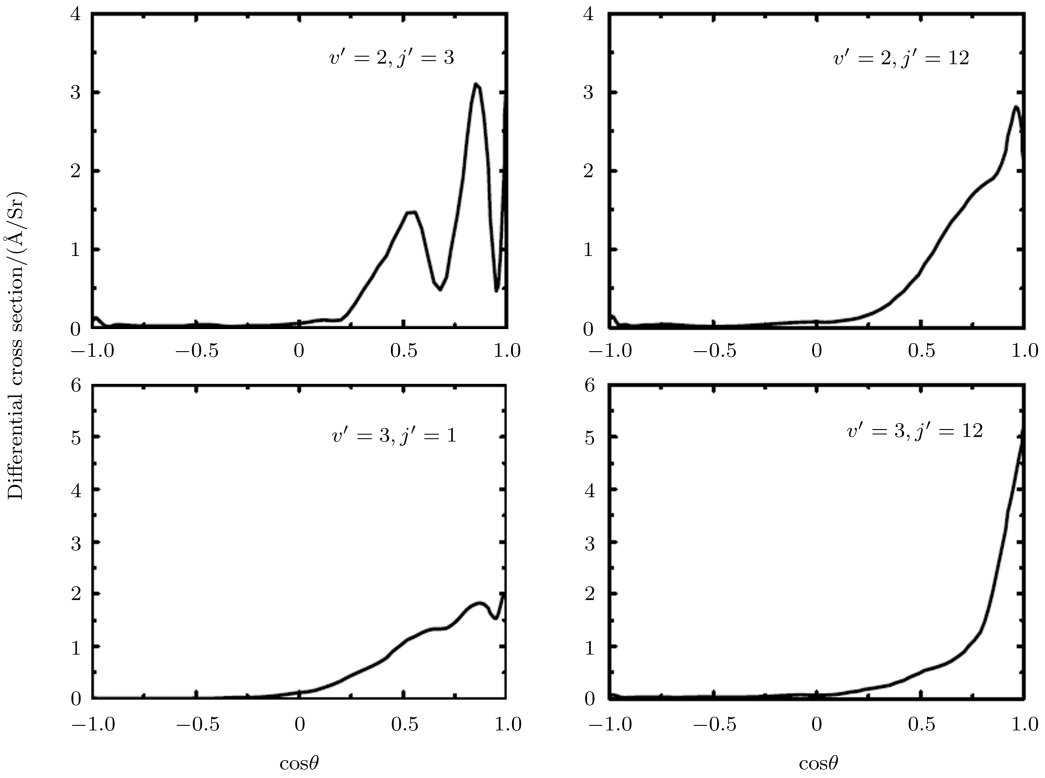
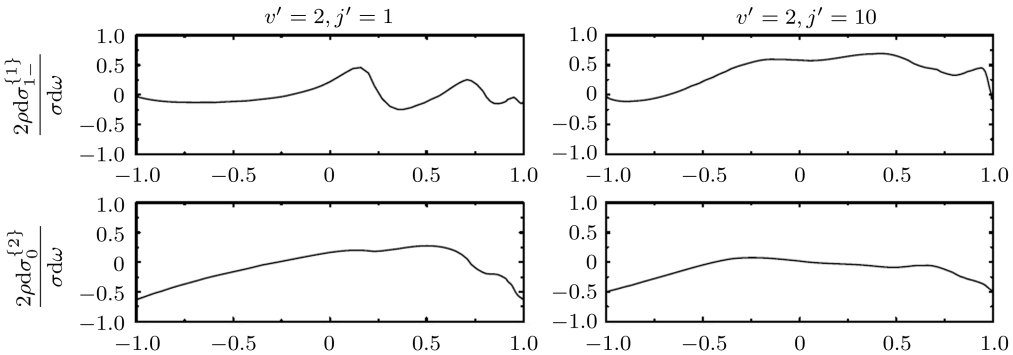


Fig.2. The differential cross section for H + DF($v' = 2,\ j' = 3,\ 12$; $v' = 3,\ j' = 1,\ 12$) channel at $E_{\rm col}$ = 0.87 kcal/mol.

3.1. Polarization-dependent differential cross sections (PDDCSs)

The real nonvanishing PDDCSs with $k \leq 2$ have been calculated for every rovibrational state of the DF and HF products at collision energies of 0.52 kcal/mol and 0.87 kcal/mol, using the QM methodologies described in the previous section. Figures 3 and 4 show the results obtained for some representative states of HF, with $v' = 2, j' = 1, 10$ at collision energies of 0.52 kcal/mol and 0.87 kcal/mol respectively. Obviously, no significant forward scattering can be seen in the angular distributions of four PDDCSs, they are mainly backward and sideways at $E_{\rm col}$ = 0.52 kcal/mol. As for $E_{\rm col}$ = 0.87 kcal/mol, the angular distributions are characteristic of forward and sideway scattering. It is consistent with Fig.1. The calculated PDDCSs of the DF ($v' = 2, 3, j' = 1, 12$) channel at $E_{\rm col}$ = 0.87 kcal/mol are presented in Figs.5 and 6. We observed that the PDDCSs manifest backward distributions. By comparing the two figures with Fig.2, we can obtain the same conclusion from an alternative point of view.



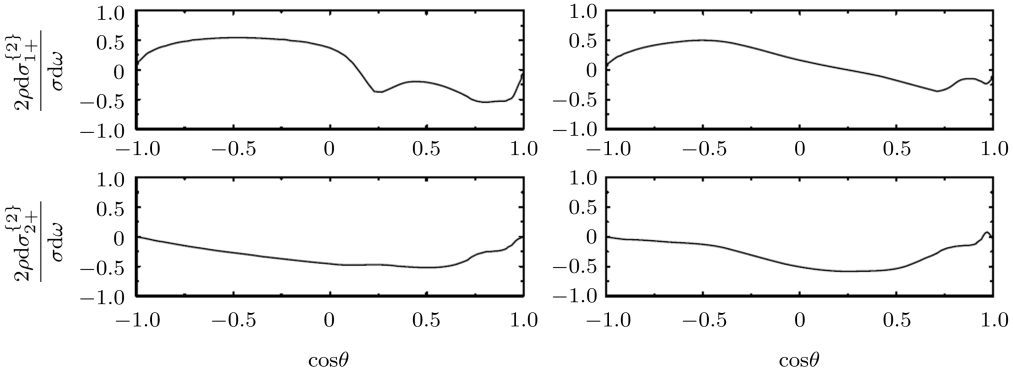


Fig.3. The PDDCSs for the F + HD($\upsilon = 0,\ j = 0$) → HF($\upsilon' = 2,\ j' = 1,\ 10$) + D reaction at $E_{\rm col}$ = 0.52 kcal/mol.

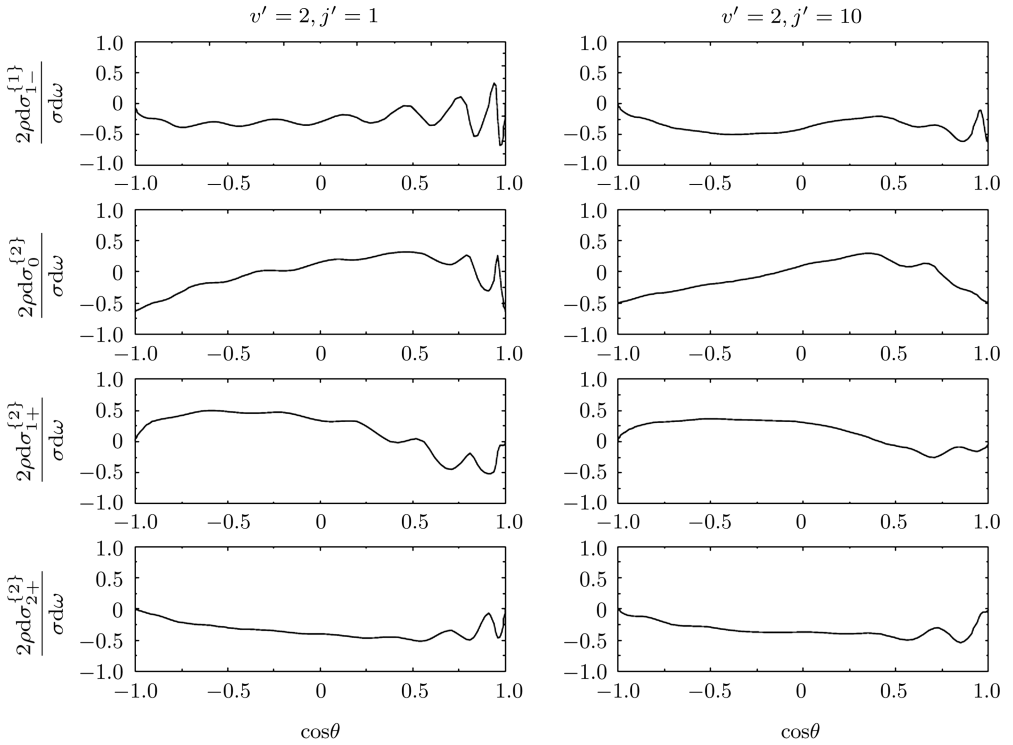
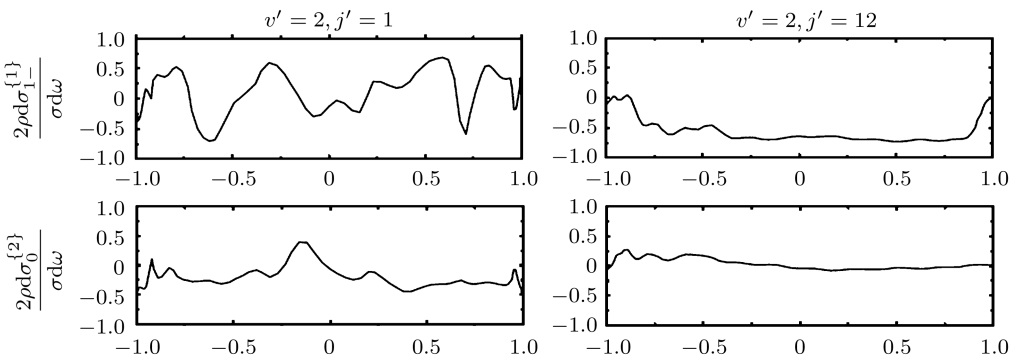


Fig.4. The PDDCSs for the F + HD($\upsilon = 0,\ j = 0$) → HF($\upsilon' = 2,\ j' = 1,\ 10$) + D reaction at $E_{\rm col}$ = 0.87 kcal/mol.



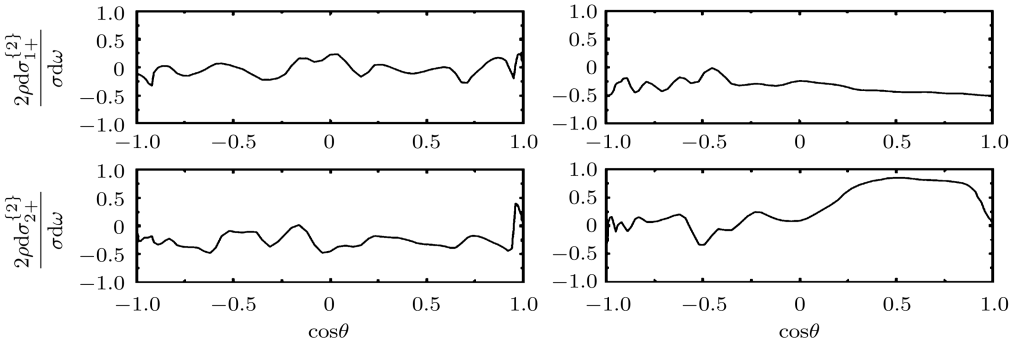


Fig.5. The PDDCSs for the F + HD($v = 0$, $j = 0$) → HF($v' = 2$, $j' = 1$, 12) + D reaction at $E_{\rm col}$ = 0.87 kcal/mol.

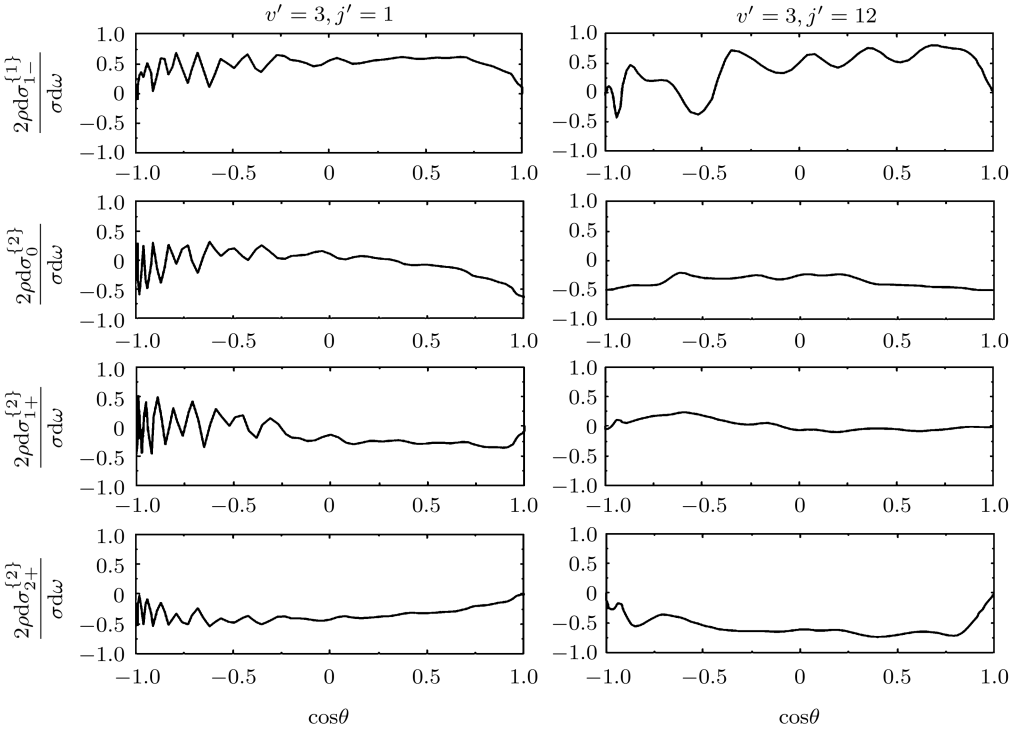
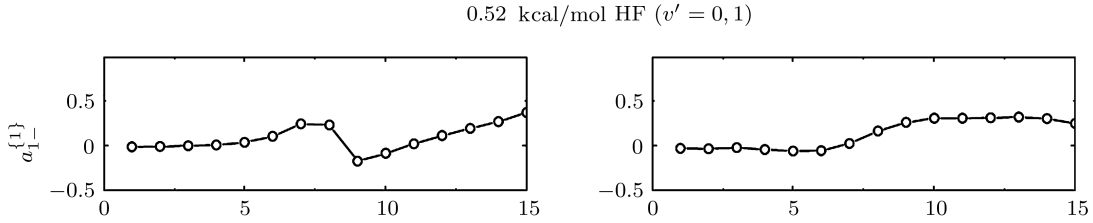


Fig.6. The PDDCSs for the F + HD($v = 0$, $j = 0$) → HF($v' = 3$, $j' = 1$, 12) + D reaction at $E_{\rm col}$ = 0.87 kcal/mol.

3.2. Polarization parameters (PPs)

In Fig.7, we present QM PPs $a_{1-}^{\{1\}}, a_{0}^{\{2\}}, a_{2+}^{\{2\}}$, and $a_{1+}^{\{2\}}$ for HF($v' = 0, j'; v' = 1, j'$) at collision energy of 0.52 kcal/mol. The four QM PPs for HF($v' = 2, j'$) at collision energies of 0.52 kcal/mol and 0.87 kcal/mol are given in Fig.8. While, figure 9 depicts the PPs for HF($v' = 0, j'; v' = 1, j'$) at $E_{\rm col}$ = 0.87 kcal/mol. Additionally, the calculated results for DF at $E_{\rm col}$ = 0.87 kcal/mol are shown in Figs.10 ($v' = 0, j'; v' = 1, j'$) and 11 ($v' = 2, j'; v' = 3, j'$).



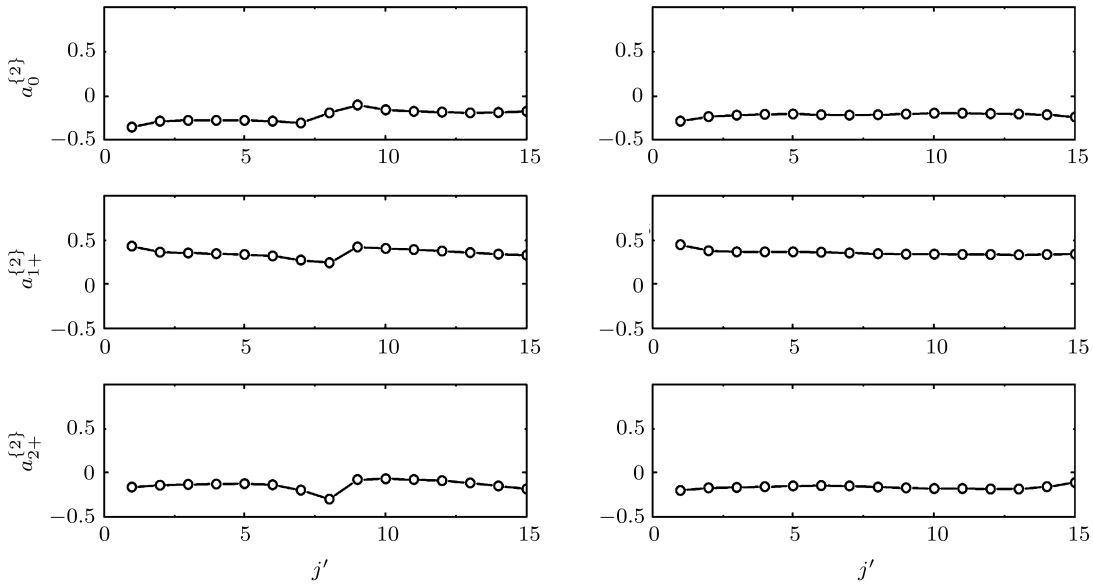


Fig.7. The PPs for the F + HD(v = 0, j = 0) → HF(v' = 0, 1) + D reaction at $E_{\rm col}$ = 0.52 kcal/mol. Left: v' = 0. Right: v' = 1.

A closer inspection of the values of the PPs reveals more specific information about the j' polarization which can be summarized as follows:

(a) HF($v' = 0, j'; v' = 1, j'; v' = 2, j'$) at collision energy of 0.52 kcal/mol

When $j' < 6$, $a_{1-}^{\{1\}}$ equals zero. With the increasing of j', the values of $a_{1-}^{\{1\}}$ vary from positive to negative and comeback to positive again for $v' = 0$ and 2. This implies that j' orientation changes from parallel to anti-parallel, then parallels to the y axis again. For $v' = 1$, the positive values of $a_{1-}^{\{1\}}$ indicate that j' orientation parallels to the y axis.

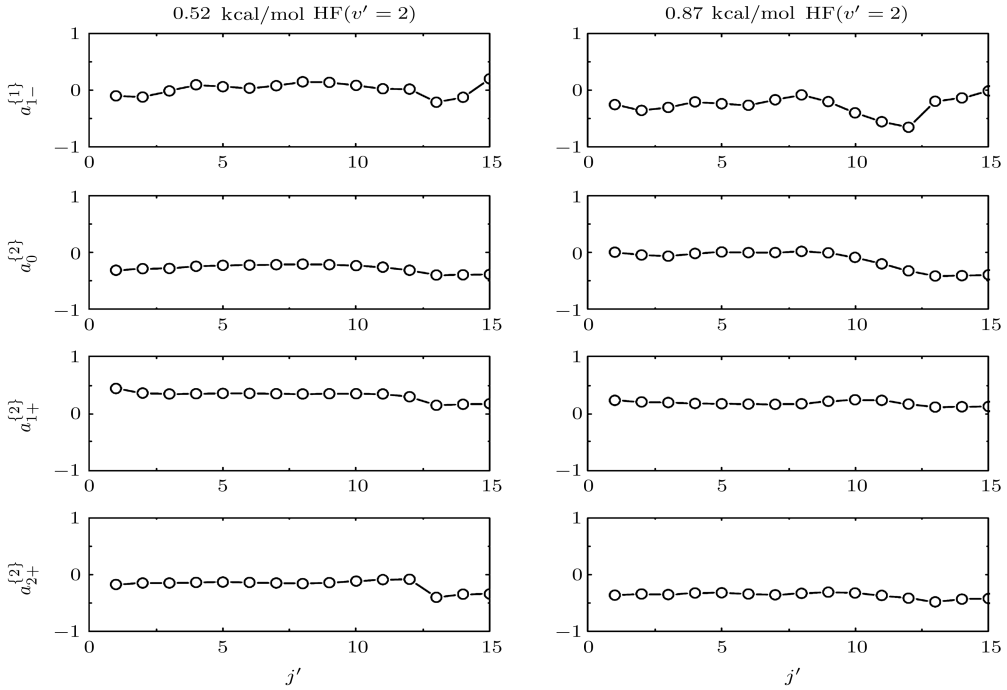


Fig.8. The PPs for the F + HD(v = 0, j = 0) → HF(v' = 2) + D reaction at $E_{\rm col}$ = 0.52 kcal/mol and 0.87 kcal/mol.

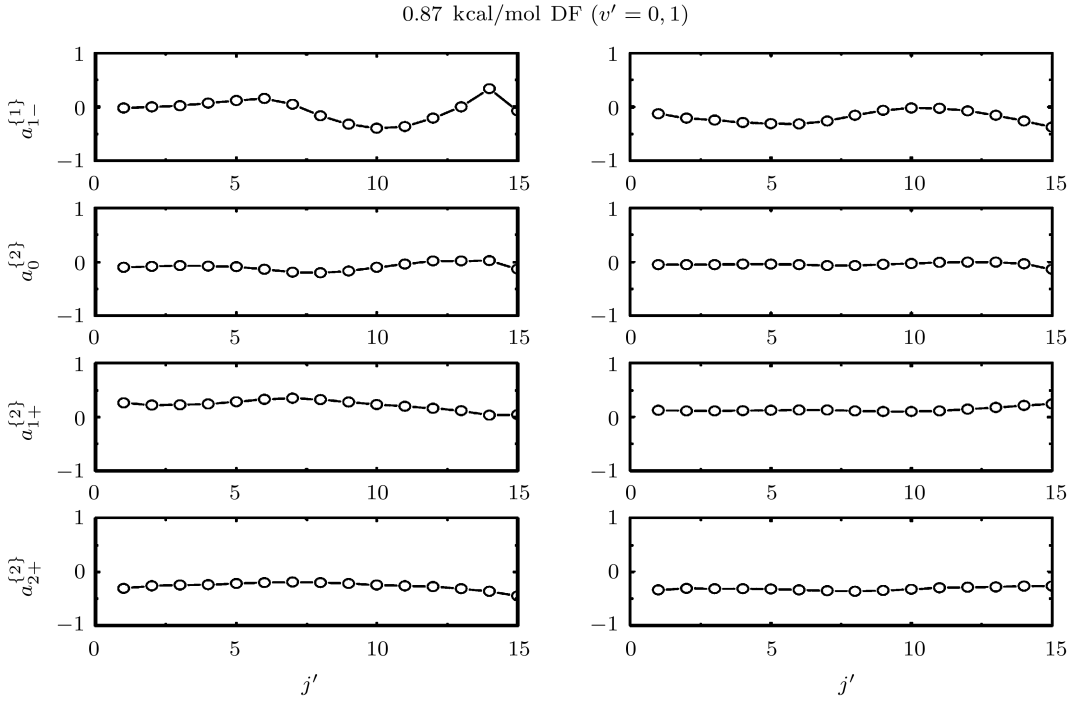


Fig.9. The PPs for the F + HD(v = 0, j = 0) → HF(v' = 0, 1) + D reaction at $E_{\rm col}$ = 0.87 kcal/mol. Left: $v' = 0$. Right: $v' = 1$.

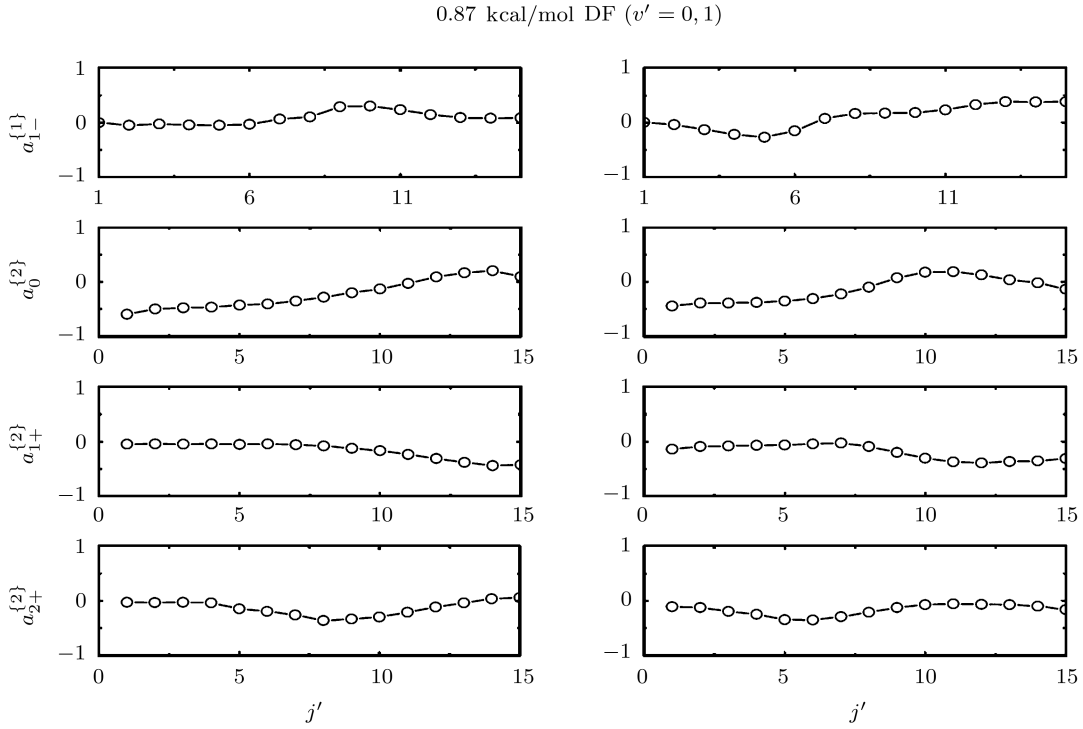


Fig.10. The PPs for the F + HD(v = 0, j = 0) → DF(v' = 0, 1) + H reaction at $E_{\rm col}$ = 0.87 kcal/mol. Left: $v' = 0$. Right: $v' = 1$.

The values of $a_0^{\{2\}}$ are negative, it means that the rotational angular momentums align along the z axis for all j'. The small positive values of $a_{1+}^{\{2\}}$ indicate a slight preference for alignment along the $x + z$. The values of $a_{2+}^{\{2\}}$, which are systematically negative, denote a clear preference for alignment along the y axis.

(b) HF($v' = 0, j'; v' = 1, j'; v' = 2, j'$) at collision energy of 0.87 kcal/mol

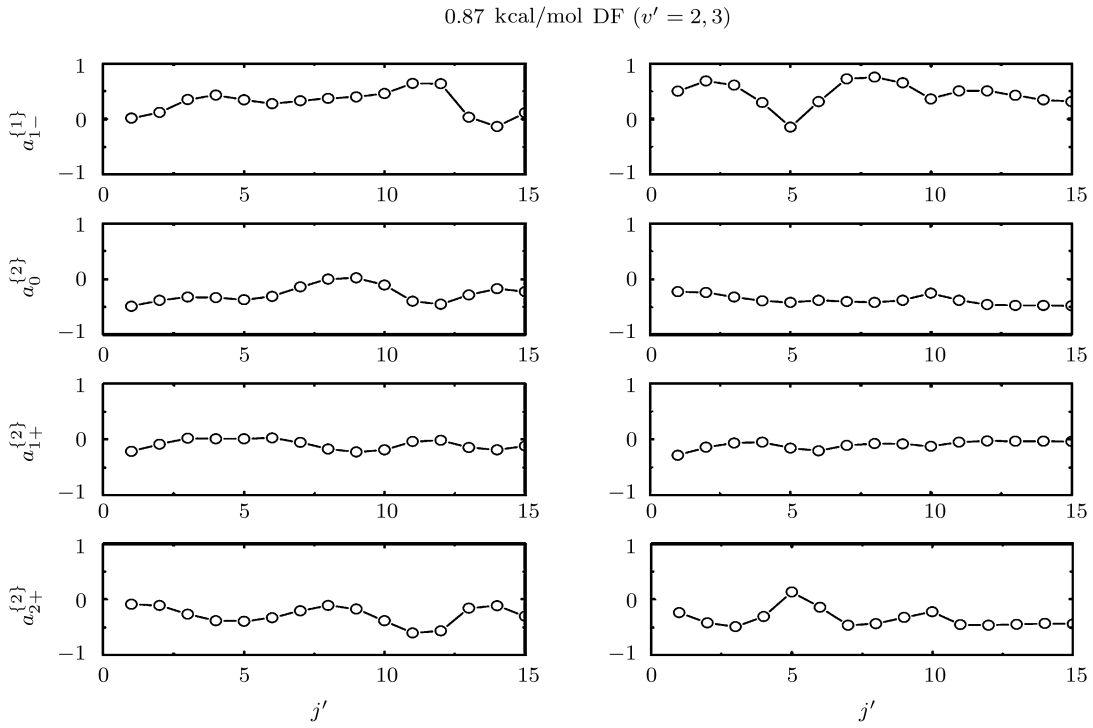


Fig.11. The PPs for the F + HD(v = 0, j = 0) → DF(v' = 2, 3) + H reaction at $E_{\rm col}$ = 0.87 kcal/mol. Left: $v' = 2$. Right: $v' = 3$.

The values of $a_{1-}^{\{1\}}$ are negative for $v' = 1$ and $v' = 2$, but there is a neat orientation of j' along the negative y axis (perpendicular to the $\boldsymbol{k} \times \boldsymbol{k}'$ scattering plane). For $v' = 0$, when $j' < 4$, $a_{1-}^{\{1\}}$ equals zero. The values of $a_{1-}^{\{1\}}$ vary from positive to negative and comeback to positive with the increasing of j'. It implies that j' orientation changes from parallel to anti-parallel, then parallels to the y axis.

Also for $v' = 0$, $a_{0}^{\{2\}}$ has small negative values which almost equal zero, it means that j' has a slight preference for alignment along the z axis. As for $v' = 1$, $a_{0}^{\{2\}}$ nearly equals zero. And for $v' = 2$, when $j' > 10$, the negative $a_{0}^{\{2\}}$ increases with the increase of j'; when $j' \geq 13$, it is close to -0.5, so this hints that the trend of j' has a slight preference for alignment along the z axis.

The small positive values of $a_{1+}^{\{2\}}$ indicate a slight preference for alignment along the $x + z$. Specially, when $v' = 3$, $a_{1+}^{\{2\}}$ is close to 0.5, it demonstrates that angular momentum aligns along the y axis. The values of $a_{2+}^{\{2\}}$, systematically negative, denote a clear preference for alignment along the y axis.

(c) DF($v' = 0, j'; v' = 1, j'; v' = 2, j'; v' = 3, j'$) at $E_{\rm col} = 0.87$ kcal/mol

For $v' = 0$ and $v' = 1$, all the PPs have the similar trend varying with the increase of j' except for $a_{1-}^{\{1\}}$. When $v' = 0$ and $j' < 6$, $a_{1-}^{\{1\}}$ equals zero, otherwise, it has a small negative value, so the orientation of j' inclines to anti-parallel to the y axis. For $v' = 1$, the value of $a_{1-}^{\{1\}}$ varies from zero to a small negative one, then becomes positive with the increase of j', this reveals that the orientation changes from anti-parallel to parallel to the y axis.

The value of $a_{0}^{\{2\}}$ increases from -0.5 to positive one, then it decreases. The alignment of j' changes along or perpendicular to the z axis corresponding to the positive or negative values of $a_{0}^{\{2\}}$. The increasing negative value of $a_{1+}^{\{2\}}$ indicates that the alignment of j' is enhanced along $x - z$. Moreover, the negative value of $a_{2+}^{\{2\}}$ denotes a preference for alignment along the y axis.

For $v' = 2$ and $v' = 3$, the PPs have the similar trend of angular distribution. The values of $a_{1-}^{\{1\}}$ have different maxima and minima, so the orientation of j' inclines to parallel to the y axis, especially when $a_{1-}^{\{1\}} \geq 0.5$. The values of $a_{0}^{\{2\}}$ vary from negative to positive, thus the rotational angular momentums of DF have preference for alignment along the z axis. The small negative values of $a_{1+}^{\{2\}}$ indicate a slight pref-

erence for alignment along the $x - z$. The values of $a_{2+}^{\{2\}}$, which are systematically negative, denote a clear preference for alignment along the y axis.

4. Conclusions

In summary, to study the stereodynamic properties of the F + HD reaction, a time-independent quantum scattering calculation has been carried out at the collision energies of 0.52 and 0.87 kcal/mol. The differential cross sections are found to be consistent with other theoretical results. The polarization-dependent differential cross sections and polarization parameters are also obtained, and the orientations and alignments of product angular momentums are discussed in detail with them. To the best of our knowledge, it is the first quantum stereodynamics calculation of the two quantities for the title reaction. It should be helpful for providing us much more information about stereodynamics in other reaction system.

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