

COMMUNICATION

Theoretical Calculation of Vector Correlations of the Reaction $D(^3S) + HS \rightarrow S + DH$

$D(^3S) + HS \rightarrow S + DH$

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Received 8 Oct 2013; Accepted (in revised version) 15 Nov 2013

Abstract: Quasi-classical trajectory calculations were performed to study the abstraction and exchange processes in the title reaction on an accurate $^1A'$ potential energy surface [J. Chem. Phys. 116, 4124 (2002)]. The alignment and orientation of the product DH and the polarized differential cross-section have been calculated at collision energies of 35 kcal/mol. Moreover, the effect of vibrational excitation on the alignment and the orientation of product molecule have also been obtained and discussed.

AMS subject classifications: 81U10, 81V45

Keywords: Quasi-classical trajectory, Vibrational excitation, Alignment, Orientation

From the last two decades, the $S(^1D, ^3P) + H_2$ reactions and its reverse reaction as well as the isotopic variants have received considerable interest due to their important role in combustion and atmospheric chemistry. Many dynamic properties such as integral cross sections and differential cross sections [1-3], product translational energy distribution and isotope branching ratio [4-7], potential energy surface [8-10], as well as the remarkable nonadiabatic effect have been extensively studied [11-14]. Very recently, Guo and coworkers employed the QCT method to study the integrated cross-sections [15-16] and stereodynamics of abstract reaction $D+DS$ on the $^3A''$ potential energy surface (PES). The results indicated that the product rotational angular momentum vectors are not only aligned, but also oriented. Lv [17-18] et al studied the exchange reaction $H + HS$ and $D+DS$ reactions on the $^1A'$ potential energy surface (PES) by using the quantum time dependent wave packet (TDWP) and quasiclassical trajectory (QCT) calculations. However, to the best of our knowledge, up to now there is still no correlative work to study the stereodynamics properties of the $D+HS$

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reaction on $^1\text{A}'\text{PES}$. In this paper we mainly focus our attention on energy dependence on stereodynamics properties of this reaction restricted on $^1\text{A}'\text{PES}$.

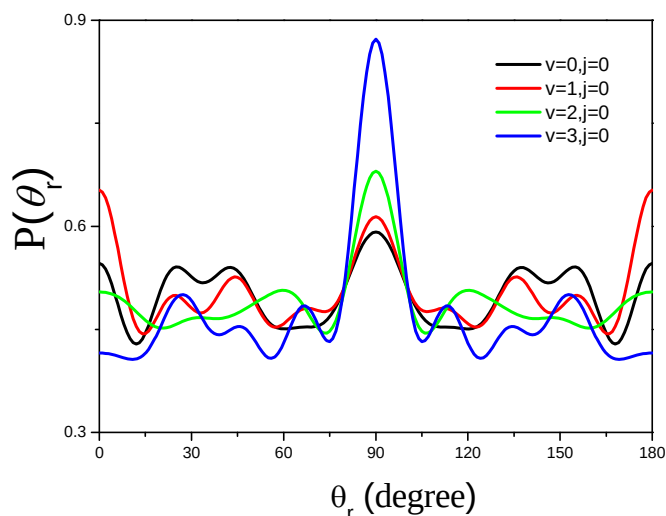


Figure 1: The distributions of $p(\theta_r)$ of the DH product from the reaction $\text{D}(^2\text{S}) + \text{HS}$ ($v=0,1,2,3$, $j=0$) $\rightarrow \text{S} + \text{DH}$ at the collision energy of 35 kcal/mol.

The center-of-mass (c.m.) frame is utilized in our calculations. The CM frame is used in the present study. The z-axis is parallel to the reagent relative velocity vector $\mathbf{k}$, while the xz-plane (also called the scattering plane) contains $\mathbf{k}$ and $\mathbf{k}'$ with $\mathbf{k}'$ on the $x \geq 0$ half plane. The y-axis is perpendicular to the scattering plane, θ_r is the angle between $\mathbf{k}$ and $\mathbf{j}'$, Φ_r is the dihedral angle between the scattering plane and the plane containing $\mathbf{k}$ and $\mathbf{j}'$, θ_r is the angle between the $\mathbf{k}'$. In the c.m. frame, the product rotational polarization can be depicted through angular distributions $P(\theta_r)$, $P(\Phi_r)$ and polarization-dependent generalized differential cross section (PDDCS). The product rotational polarization for the title reactions is investigated, using the stereo-QCT procedure which was developed by Han et al.^[19-22]. Each reaction runs 100 000 trajectories and the integration step size is set as 0.1 fs to guarantee the conservation of total angular momentum and total energy. The calculations of the product rotational polarization with the initial rotational quantum number $j=0$ and initial vibrational quantum number $v=0, 1, 2, 3$. The collision energy is 35 kcal/mol and the initial collision length is 15 Å for each reaction.

As we know, the distribution of $P(\theta_r)$ describes the $\mathbf{k}-\mathbf{j}'$ correlation and the distributions of $P(\theta_r)$ for product DH at collision energies of 35 kcal/mol are presented in Fig. 1. As can be seen from Fig. 1, the $P(\theta_r)$ distributed at all scattering angle from 0-180° and are symmetric with respect to 90° for $v=0$ and 1, which indicates there is no preferentially direction the product aligned. However, with the increasing vibrational quantum numbers, it is clearly see that the largest peaks of $P(\theta_r)$ are at 90° for $v=2$ and 3, which directly demonstrates that the

product show obviously polarization align the perpendicular direction to relative velocity k . Furthermore, the peak of $P(\theta_r)$ at 90° becomes narrower and higher with the vibrational excitation. It can be concluded that the vibrational excitation has large effect on the distributions of $P(\theta_r)$.

The dihedral angle distributions $P(\Phi_r)$ shown in **Fig. 3** describe the k - k' - j' correlation. As can be seen from **Fig.3**, the distributions of $P(\Phi_r)$ are relatively broad, but peaks of $P(\Phi_r)$ around 90° and 270° are much larger than those of other angles for four vibrational states especially at $v=3$, which indicates that the rotational angular momentum vector of the product DH is mainly aligned along y-axis of the CM frame. In addition, the distributions of $P(\Phi_r)$ are tend to be asymmetric with respect to the k - k' scattering plane (or about $\Phi_r = 180^\circ$), directly reflecting preferred orientation of the product DH. For example, the appearance of the peaks at 90° is higher than that at 270° verified that the product rotational angular momentum vectors aligned along the y-axis.

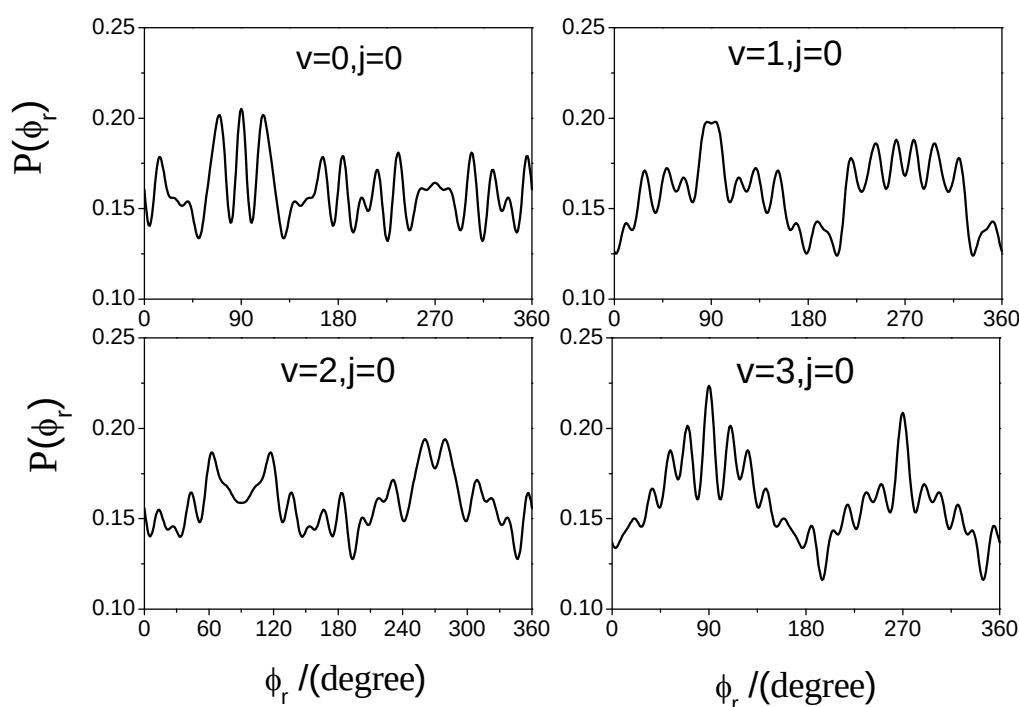


Figure 2: The distributions of $p(\Phi_r)$ of the DH product from the reaction $D(^2S) + HS (v=0,1,2,3, j=0) \rightarrow S + DH$ at the collision energy of 35 kcal/mol.

The polarization-dependent differential cross sections $((2\pi/\sigma)(d\sigma_{00}/d\omega_t))$ named $PDDCS_{00}$, which is simply proportional to the differential cross-section (DCS), only describe the k - k' correlation or the scattering direction of the product. For $v=0$ and 1, one could observe that the distributions of $PDDCS_{00}$ have a roughly symmetric behavior, with a small sideways scattering and a forward peak which is similar in magnitude to the backward one. This

behavior is usually observed for a reaction involving a long-lived intermediate complex in the collision process. However, with the increasing of vibrational excitation, the distributions of PDDCS₀₀ are clearly dominated by a strong forward peak and a much smaller backward scattering. This asymmetric c.m. angular distribution is consistent with a reaction which does not proceed via a long-lived intermediate complex and the preference for forward scattering simply indicates that the complex breaks before completing a rotation defined. One can conclude that the PDDCS₀₀ is dependent on the vibrational excitation and different mechanism is involved in reaction when the HS is excited to $v=2$ and 3. Further research is requested to reveal the more detailed mechanism of the title reaction.

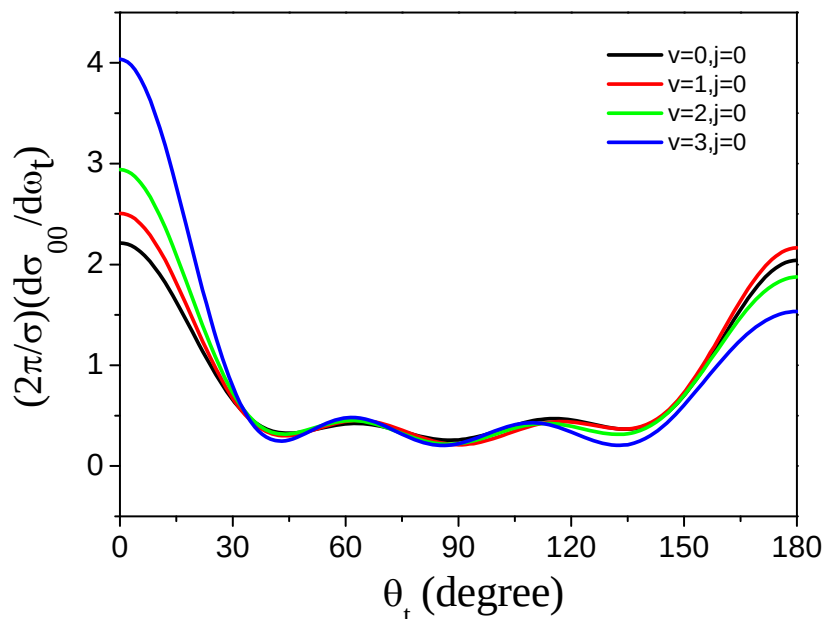


Figure 3: The distributions of the polarization-dependent differential cross sections $((2\pi/\sigma)(d\sigma_{00}/d\omega_t))$ of the DH product from the reaction $D(^2S)+HS$ ($v=0,1,2,3$ $j=0$) $\rightarrow$ S + DH at the collision energy of 35 kcal/mol.

Acknowledgement

The support of the Natural Science Foundation of China (No.11204392 and No.11047125) is gratefully acknowledged.

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