

Quasiclassical Trajectory Study of Stereodynamics for Exchange Reactions $H' (D') + H (D) S$

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Abstract. Product Polarizations for the exchange reaction $H'+HS$ and its isotopic variants on an accurate $1A'$ potential energy surface have been studied at collision energies of 10 kcal/mol by using the quasi-classical trajectory method (QCT). Product rotational angular momentum distributions $P(\theta_r)$ and $P(\phi_r)$ are calculated in the center-of-mass (CM) frame. Moreover, three generalized polarization-dependent differential cross sections (PDDCSs) are also computed. The results demonstrated that the isotopic effect displays sensitive effect on the product vector correlations. The reaction mechanism was discussed based on the properties of stereodynamics and the reactive trajectories.

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Key words: stereodynamics; Isotopic Effects; Quasiclassical Trajectory; Exchange Reaction.

1 Introduction

The importance of vector correlations in reaction dynamics was first pointed out by Herschbach and coworkers based on the fact that chemical reactions are intrinsically anisotropic [1]. The vector and vector correlations include those of reagent $k-j$, $j-k-k'$ correlations and those of product $k-j'$, $k-k-j'$ correlations, where k/k' and j/j' denotes the relative velocity of reagent/product and the reagent/product rotational angular momentum in the center of mass (CM) frame. The growing interest in the field is largely due to the advent of new experimental techniques and theoretical methods. Experimentally, the availability of new experimental methods has made it possible to measure and probe the product state-resolved rotational polarization and $k-k'-j'$ correlation, such

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as Doppler resolved laser induced fluorescence or resonance enhanced multiphoton ionization time-of-flight techniques. In order to easily interpret the vector correlations of the experimental measurements and clearly depict the corresponding stereodynamical picture, both the quasi-classical trajectory (QCT) [2-5] and the quantum scattering methods [6-7] have been developed to determine the product vector correlations. To date, the vector correlations has been widely and successfully studied in many stereodynamics calculations [8-15].

The gas-phase S (1D , 3P) + H₂ reaction and its reverse reaction as well as the isotopic variants act as an important role in combustion and atmospheric chemistry, which have received considerable interest from last two decades. In previous work, many scalar properties such as product translational energy distribution [16], integral cross sections, differential cross sections and isotope branching ratio [17-23], potential energy surface [24-26], as well as the remarkable nonadiabatic effect have been extensively studied. [27-28] Recently, Guo and coworkers employed the QCT method to study the stereodynamics of abstract reaction D+DS on the $^3A''$ potential energy surface (PES), which has an energy barrier in the reaction path [29]. They have found that the product rotational angular momentum vectors are not only aligned, but also oriented. However, to the best of our knowledge, up to now there is still no correlative work to study the isotopic effect on stereodynamics properties of the H+HS reaction on $^1A'$ PES. In this paper we mainly focus our attention on isotopic effect on stereodynamics properties of this reaction restricted on $^1A'$ PES.

2 Theory

The present calculations were performed by applying a standard QCT-stereodynamics procedure which has been successfully used to study a great deal of collision reactions. The center-of-mass (c.m.) frame is utilized in our calculations. The z-axis is parallel to the reagent relative velocity vector k , while the xz-plane (also called the scattering plane) contains k and k' with k' on the $x \geq 0$ half plane. The y-axis is perpendicular to the scattering plane, θ_r is the angle between k and j' , ϕ_r is the dihedral angle between the scattering plane and the plane containing k and j' , θ_t is the angle between k and 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 sections (PDDCSs). The product rotational polarization for the title reactions is investigated, using the stereo-QCT procedure which was developed by Han *et al.* [2-5]. 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 $v=0$. The collision energy is 10kcal/mol and the initial collision length is 15 Å for each reaction.

The general theory of the product rotational polarization is standard, and here we