

Effect of isotope substitution on the stereodynamics for $O+H(D)Br \rightarrow OH(D)+Br$ reactions

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Abstract. The influence of the isotope substitution on the dynamics of the title reactions is investigated using the quasi-classical trajectory method based on the potential energy surface for the X^1A' ground singlet state of HOBr system. Apparent differences on the stereo-dynamic properties are discovered between the title reactions. These discrepancies are mainly due to the unequal reduced masses of the reactants and different zero-point energies of the transition state, which affect the vector properties of the title reactions.

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1 Introduction

Over the past decade, some significant achievements have been made on the side of theoretical and computational chemistry. One of the progresses is that the quasi-classical trajectory (QCT) method has been widely carried out to analyze the dynamics of chemical reactions, especially for the reaction systems with large mass [1, 2]. Meanwhile, Han *et al.* [3] developed the stereo-dynamics QCT method to cope with the product rotational polarization. So far, many chemical reactions [4–12] have been studied for their product rotational polarization. Moreover, this kind reaction of $O + HX \rightarrow OH + X$ ($X = F, Cl, Br, I$) not only is the elementary reaction with Heavy-Light-Heavy (HLH) mass system that makes the product rotation strongly aligned about the direction of the relative velocity, but also contains the important atom shift process about H [13].

Recently, for the reaction $O + HBr \rightarrow OH + Br$, many studies for the presented interesting dynamical features have been done, theoretically and experimentally. On the experimental side, Ruscic and Berkowitz have successfully ciphered the heat of formation of HOBr and the dissociation energy of HO–Br [14]. From the theoretical point of view, Tang *et al.* [15] have

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successfully employed the three-dimensional time-dependent quantum wave packet method to study the scalar properties of the reaction such as initial state-selected reaction probabilities, reactive cross sections and thermal rate constant. Additionally, the potential energy surface (PES) for the X^1A' singlet state of HOBr system was recently constructed by Peterson [16].

In our previous work, we have studied the vector properties of reaction $O + HBr \rightarrow OH + Br$. It is well known that the isotope effect plays key roles in the deduction of the chemical reaction mechanics and the research of intermolecular interaction. To the best of our knowledge, few studies are reported yet for the isotope substitution of the title reactions. Such an inquiry is the subject of this paper. In order to realize the isotope effect on the reaction, we utilize the QCT calculations to investigate $O + HBr$ reaction and its isotope variant on the same singlet PES.

This paper is organized as follows. In Section 2, the QCT calculation is briefly outlined. The results which will be an important consideration are presented and discussed in Section 3. In Section 4, the discussion and its implications are presented.

2 Computational method

The X^1A' ground singlet PES applied to this paper was determined by Peterson employing the method of highly correlated MRCI and explicit basis set [17]. The detailed information such as *ab initio* data and analytical function form of the PES can be referred to in Ref. [18].

The computational method of QCT in this study is the same as the one adopted in Ref. [19, 20]. In the calculations, the classical Hamilton's equations are integrated in three dimensions. According to the product rotational polarization, we mainly concentrate on discussing the isotope effect on the reaction. We set the initial rotational quantum $j=0$ and initial vibrational quantum $v=0$. The collision energy of the title reactions is chosen as 0.3 eV. Each reaction runs 10000 trajectories and the integration step size is set as 0.1 fs to guarantee the conservation of the total angular momentum and total energy.

The product polarization calculations we carry out is well-rounded by Han and coworkers [21]. Here we just introduce the details connected with our existing work. In the center-of-mass (CM) frame shown in Fig. 1, the relative velocity vector \mathbf{k}' of the reactant is parallel to the z -axis and the x - z plane which is the scattering plane contains the initial and final relative velocity vectors, \mathbf{k} and \mathbf{k}' . The scattering angle θ_t is the angle between the reactant relative velocity and product relative velocity. θ_r and ϕ_r represent, respectively, the polar and azimuthal angle of the product rotational angular momentum \mathbf{j}' .

The vector correlation of $\mathbf{k}-\mathbf{j}'$ is the most common. The polar angle distribution function rewriting the correlation of $\mathbf{k}-\mathbf{j}'$ can be expanded in a series of Legendre polynomials and the expanding coefficients are called alignment (k is even) and orientation (k is odd) parameter. The dihedral angle distribution function $P(\phi_r)$ describing $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation can be unfolded in Fourier series. The $P(\theta_r, \phi_r)$ as the function of angles θ_r and ϕ_r of \mathbf{j}' is used to depict the space distribution of the product rotational momentum.