Quasi-Classical Trajectory Studies of the Stereodynamics of the Reaction $O + HCl \rightarrow ClO + H$

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Abstract—The stereodynamics of the $O + HCl \rightarrow ClO + H$ reaction are investigated by quasi-classical trajectory (QCT) method. The calculations are carried out on the ground $^1A'$ potential energy surface (PES). The orientation and alignments of the product rotational angular momentum for the title reaction are reported. The influence of collision energy on the product vector properties is also studied in the present work. Four $(2\pi/\sigma)(d\sigma_{00}/d\omega_0)$, $(2\pi/\sigma)(d\sigma_{20}/d\omega_0)$, $(2\pi/\sigma)(d\sigma_{22}/d\omega_0)$, and $(2\pi/\sigma)(d\sigma_{21}/d\omega_0)$ have been calculated in the center of mass frame.

Keywords: quasi-classical trajectory studies, stereodynamics of reaction $O + HCl$.

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INTRODUCTION

Over the past 40 years the dynamics of the reaction $O(1D) + HCl$ has been extensively investigated both from the experimental [1–9] and theoretical [10–24] viewpoint. One reason is due to its important role in atmospheric chemistry [25, 26]. Another reason is due to the presence of two competitive product channels which are $O(1D) + HCl \rightarrow OH + Cl$ and $ClO + H$. From the experimental viewpoint, the branch ratio of the two different product channels ($O(1D) + HCl \rightarrow OH + Cl$ and $ClO + H$) was measured by Matsumi et al. [1]. The angular distributions of the ClO and OH products were measured by Balucani et al. [2] and Alexander et al. [3] respectively, using different experimental methods. In more recent experiments the doubly differential cross sections of $Cl(2P)$ for $O(1D) + HCl \rightarrow OH + Cl$ and $ClO + H$ was measured by Peterson et al. [11]. The vector correlations represent an interesting probe to understand the stereodynamics underlying chemical reactions in a chemical reaction, [27, 28]. Among others, the vector properties, such as the relative velocities of the reagent and product and the product rotational angular momentum of a chemical reaction can provide valuable information about chemical reaction stereo-dynamics [29]. However, for the reaction of $O(1D) + HCl \rightarrow ClO + H$, the stereo dynamics has not been studied. In this paper, we focused on the vector properties of this reaction and the influence of collision energy and rotational excitation on the stereo-dynamics.

THEORY

Quasi-Classical Trajectory Calculations

The vector correlations represent an interesting probe to understand the stereodynamics underlying chemical reactions in a chemical reaction, [27, 28]. Among others, the vector properties, such as the relative velocities of the reagent and product and the product rotational angular momentum of a chemical reaction can provide valuable information about chemical reaction stereo-dynamics [29]. However, for the reaction of $O(1D) + HCl \rightarrow ClO + H$, the stereo dynamics has not been studied. In this paper, we focused on the vector properties of this reaction and the influence of collision energy and rotational excitation on the stereo-dynamics.

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The calculations of $O(1D) + HCl$ and its isotopic reactions have been performed on the PSB2 PES [14], which is an improved version of the PSB PES constructed by Peterson, Skokov and Bowman [13]. The details of the PSB2 PES can be found in [11, 12, 14].

The calculation method of QCT is the same as the one used in [30–33]. The classical Hamilton’s equations are numerically integrated in three dimensions. To be able to compare the experimental and theoretical results from other studies, the collision energies are set at 3, 6.4, and 12.2 kcal/mol, respectively, in the present work. We have carried out the calculations of the product rotational polarization with the initial vibrational number $v = 0$ and the initial rotational quantum number $j = 5$. The initial collision length is 15 Å for all these reactions. A batch of 10 000 trajecto-
Product Rotational Polarization

The general theory of the product rotational polarization is standard [30–35], and here we only provide a simple description relevant to the present work. The reference frame used in this work is the center-of-mass (CM) frame, which is shown in Fig. 1. The reagent relative velocity vector \( \mathbf{k} \) is parallel to the \( z \) axis and the \( x-z \) plane is the scattering plane containing the initial and final relative velocity vectors, \( \mathbf{k} \) and \( \mathbf{k}' \). The angle \( \theta \) is the so-called scattering angle between the reagent relative velocity and the product relative velocity. The angles \( \theta \) and \( \phi \) are the polar and azimuthal angles of the final rotational angular momentum \( \mathbf{j}' \).

The distribution function \( P(\theta) \) and the dihedral angle distribution function \( P(\phi) \) described the \( \mathbf{k} \)–\( \mathbf{j}' \) and \( \mathbf{k}' \)–\( \mathbf{j}' \) correlations, respectively. The function \( P(\theta) \) can be expanded in a series of Legendre polynomials as [30, 31]

\[
P(\theta) = \frac{1}{2} \sum_k (2k + 1)a_0^{(k)} P_k(\cos \theta),
\]

where

\[
a_0^{(k)} = \int_{0}^{\pi} P(\theta) P_k(\cos \theta) \sin \theta \, d\theta = \langle P_k(\cos \theta) \rangle. \tag{2}
\]

The expanding coefficients \( a_0^{(k)} \) are called the orientation (\( k \) is odd) or alignment (\( k \) is even) parameters.

The dihedral angle distribution function \( P(\phi) \) can be expanded in a series of Fourier series as

\[
P(\phi) = \frac{1}{2\pi} \left[ 1 + \sum_{\text{even}, n \geq 2} a_n \cos n\phi \right] + \sum_{\text{odd}, n \geq 1} b_n (\sin n\phi), \tag{3}
\]

where

\[
a_n = 2 \langle \cos n\phi \rangle, \tag{4}
\]

\[
b_n = 2 \langle \sin n\phi \rangle. \tag{5}
\]

In this calculation, \( P(\theta) \) and \( P(\phi) \) are expanded up to \( k = 18, n = 24 \), respectively, which thereby showing good convergence.

The fully correlated CM angular distribution is written as the sum:

\[
P(\omega, \omega') = \sum_{kq} \left[ \frac{k}{4\pi} \frac{d\sigma_{kq}}{d\omega} C_{kq}(\theta, \phi) \right], \tag{6}
\]

where \( d\sigma_{kq} / d\omega \) is a generalized polarization dependent differential cross-section (PDDCSs). The angles \( \omega = \theta_1, \phi_1 \) and \( \omega' = \theta_2, \phi_2 \) refer to the coordinates of the unit vectors \( \mathbf{k}' \) and \( \mathbf{j}' \) along the directions of the product relative velocity and rotational angular momentum vectors in the CM frame, respectively, while \( C_{kq}(\theta, \phi) \) are modified spherical harmonics. The detailed can be found in [30]. In the present work, \( (2\pi/\sigma)(d\sigma_{kq}/d\omega) \), \( (2\pi/\sigma)(d\sigma_{20}/d\omega) \), \( (2\pi/\sigma)(d\sigma_{21}/d\omega) \), and \( (2\pi/\sigma)(d\sigma_{22}/d\omega) \) are calculated.

RESULTS AND DISCUSSIONS

The cross sections of the product ClO at different collision energies has been studied in our previous paper [32] and was good agreement with the result of Bowman et al., which indicates the PES and our QCT calculation are properly. Here, we only focus on the stereo dynamics about this reaction, the \( P(\theta) \) distributions at three collision energies \( (E_T = 3, 6.4, \text{and } 12.2 \text{ kcal/mol}) \) of this reaction are plotted in Fig. 2.