The Non-adiabatic stereodynamics study for the reaction of Na(3s)+H$_2$ → NaH (X$^1\Sigma^+$)+H

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Abstract. A theoretical investigation of the non-adiabatic dynamics processes for the reaction Na(3s) + H$_2$ → NaH (X$^1\Sigma^+$) + H has been performed using the method of coherence switching with decay of mixing (CSDM). The integral cross sections calculated by the CSDM method are compared with the results from an adiabatic quasiclassical trajectory (QCT) calculation, which uses the same potential energy in the adiabatic representation. The product rotational polarization in non-adiabatic dynamics is presented and compared with the adiabatic results by means of the joint distributions of rotational angular momentum vectors in the scattering coordinate. It is found that the conical intersection shows significant influence on the integral cross sections of the reaction. The adiabatic effect also reduces the rotational polarization of the product NaH.

PACS: 34.35.+a, 34.50.-s, 31.50.Gh

Key words: non-adiabatic, stereodynamics, polarization.

1   Introduction

NaH$_2$ is a prototypical system for metal reactions with covalent molecules, and it has been widely studied experimentally and theoretically in many reactive or non-reactive processes. The reactions:

$$Na(3p) + H_2 \rightarrow Na(3s) + H_2(v',j') \tag{1}$$

$$Na(3p) + H_2 \rightarrow NaH(v'',j'') + H \tag{2}$$
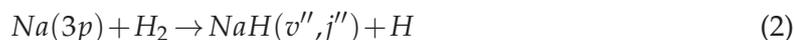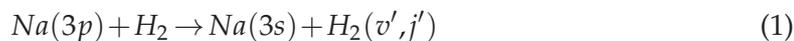
are often studied as examples of the fundamental processes of electronic-to-vibrational-and-rotational energy transfer (E-VRT) and chemical reaction with an conical intersection

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in potential energy surface [1]. The E-VRT processes may play significant role in the photochemistry of the earth's atmosphere and are of potential interest in laser chemistry. On the other hand, reactive collisions which involve transitions between different electronic states are prerequisite to a theoretical treatment of any of the more complex photochemical processes.

Most early studies for this system focus on the quenching process in reaction (1), since the energy of the conical intersection is nearly equal to the energy of the Na (3p) asymptote when NaH_2 is in C_{2v} symmetry. But the primary chemical interest is that a well occurs at this geometry and is closer to the conical intersection. As early as 1981, Botschwina *et al.* performed time-of-flight crossed molecular beam experiments on reaction (1) and determined the nonreactive dynamical properties, like the differential quenching cross section and the resulting vibrational energy distribution [2]. Years later, Devivieriedle *et al.* used coherent anti-Stokes Raman scattering (CARS) spectroscopy to measure the vibrational and rotational distribution of H_2 after it quenches the Na(3p) atom [3]. They also found new lines which do not correspond to H_2 lines are observed in the CARS spectrum. Combined with the *ab initio* calculations, the observed lines was attributed to the stabilized exciplex Na(3p)-HH molecule which is formed during the quenching process. More recently, Motzkus *et al.* compared the reactive and quenching behavior of the two different electronically excited sodium atoms Na(3p) and Na(4p) in a collision with H_2 using three different nonlinear optical techniques including CARS, resonance-enhanced CARS, and DFWM (degenerate four-wave mixing). They found the reactive process of reaction (2) is not a direct formation process and involves more than one step [4].

The electronic features and the accumulation of experimental data make NaH_2 system an interesting target for theoretical study. Some pioneering works were performed by semiclassical trajectory method [5-7], and then it has become possible to treat these electronically non-adiabatic processes with accurate quantum dynamics [8,9]. Although these studies provide the final rotational and vibrational energy distributions and the quenching cross sections, most pervious works only focus on unreactive quenching process at low collision energy or the predissociation of the of NaH_2. In this work we calculated the stereodynamics properties of reaction $Na(3s) + H_2 \rightarrow NaH(X^1\Sigma^+) + H$, and the non-BO effect is also taken into consideration. We compared the non-adiabatic results with the adiabatic quasi-classical trajectory (QCT) calculations. This calculation focus on the impact of the conical intersection on the steredynamics properties of the state reaction.

Potential energy surfaces and their coupling are the start point of the dynamics studies of a non-adiabatic system. Ben-Nun *et al.* reported a four-state potential energy matrix based on molecular orbital theory and parameterized to *ab initio* calculations. But in this paper we used a two-state potential matrix called Surface set 6 [10], which is based on an eight-state semiempirical diatomics-inmolecules (DIM) potential matrix [4,5]. Surface set 6 has an infinite number of continuous derivatives and is designed to have the correct behavior in the region of the conical intersection. The coherent switching with decay of