Quantum dynamics study of H exchange reaction of H′(^{2}S) + CH(X$^2\Pi$) → H(^{2}S) + CH′(X$^2\Pi$) and Isotope Reactions of H(^{2}S) + CH(X$^2\Pi$) → C(^{1}D) + H$_2$(X$^1\Sigma_g^+$)

Yunhui Wang, Kaiming Deng, and Ruifeng Lu[a*]

Department of Applied Physics, Nanjing University of Science and Technology, Nanjing 210094, China

Abstract. By using the time-dependent quantum wave packet method, we report a detailed dynamics study of H exchange reaction H′(^{2}S) + CH(X$^2\Pi$) → H(^{2}S) + CH′(X$^2\Pi$) and the isotope effects of H(^{2}S) + CH(X$^2\Pi$) → C(^{1}D) + H$_2$(X$^1\Sigma_g^+$) reaction on the 11A BHL potential energy surface. The reaction probabilities and integral cross sections have been obtained for the initial states $v = 0$ and $j = 1$ of the reactant molecules. The dense resonance structures in the reaction probabilities at all total angular momentums indicate complex-forming mechanisms for both C + H$_2$ and H + CH products. A comparison between the results from centrifugal sudden approximation and those from close-coupled calculations demonstrates that the Coriolis coupling effects get more and more pronounced with increasing of J for both H exchange reaction and CH decay reaction. The isotopic D substitution of reactant significantly influences the CH decay reaction. Moreover, it is revealed that the dynamical features such as partial wave contributions to the cross section are substantially different for these two channels.

PACS: 82.20.Fd, 71.15.Pd

Key words: time-dependent quantum wave packet, isotope effects, stereodynamics.

1 Introduction

Methylene molecule is an important intermediate in many organic reactions. It also plays an important role in astrochemical and combustion processes. As a prototype insertion reaction, C + H$_2$ → H + CH has drawn a great deal of attention in both experiments and theory, indicating that the reaction proceeds via the CH$_2$ intermediate which lives

---

*Corresponding author. *Email address:* `rflu@njust.edu.cn` (R.-F. Lu)

sufficiently long to permit complete energy randomization. So far, many experimental investigations of the CH_2 system have been done in understanding the kinetics [1] and dynamics [2-6]. The rotational state distribution of CH was measured and the reaction $C(^1D) + H_2$ was concluded to proceed via insertion of C(1D) into the H-H bond in a facile manner.[2] The product angular distribution measured in a molecular beam experiment shows a backward-forward symmetry, suggesting the dominance of a long-lived CH_2 complex [3]. Isotope effect has been studied for the $C(^1D) + H_2$ reaction by Fisher and co-workers, who measured the CD/CH branching ratio and estimated the thermal rate constants for reactions $C(^1D) + H_2/D_2$ [4]. The product CH is found to be highly rotationally excited, and the -doublet and spin-orbit components are equally populated in the reaction $C(^1D) + H_2$ [5]. The CH rotational distribution was also observed from $C(^1D) + H_2$ collision by laser-induced fluorescence [6], which shows that only a small fraction of the CH product is formed in its vibrationally excited state. In this experiment, insertion is the major reaction mechanism, however, the abstraction process seems to be enhanced when the vibrational quantum number of CH product varies from 0 to 1. The rate constants at the room temperature were measured for the collisions of $C(^1D)$ with H_2, HD and D_2 by standard pump-probe techniques, and the rotational distributions of CH and CD products as well as the branching ratio of CD/CH were also studied, suggesting that the long-lived complex HCH/D is formed during the reaction [7]. Moreover, the product angular and time-of-flight distributions for the reaction $C(^1D) + H_2$ were obtained by the crossed beam technique with mass spectrometric detection at the collision energy of 0.08 eV, which are in qualitative agreement with the statistical predication that the $C + H_2$ reaction behaves nearly statistically owing to the potential well is very deep [8].

The $C(^1D) + H_2$ reaction and its isotopic variants have also been intensively studied from the theoretical side. An adiabatic global potential energy surface (PES) for the first singlet state ($1^1A'$) of CH_2 system has been built by Bussery-Honvault and co-workers (BHL PES), using multireference single and double configuration interaction calculations to characterize the state [9]. As depicted schematically in Fig. 1 of the BHL PES, for the H exchange reaction $H'(^2S) + CH(X^2\Pi) \rightarrow H(^2S) + CH'(X^2\Pi)$ and the CH decay reaction $H(^2S) + CH(X^2\Pi) \rightarrow C(^1D) + H_2(X^1\Sigma_g^+)$, there exists a potential well with a depth of about 4.15 and 4.32 eV, corresponding to the $H(^2S) + CH(X^2\Pi)$ and $C(^1D) + H_2(X^1\Sigma_g^+)$ asymptotes, respectively, located at $R_{CH} = 2.09a_0$ and $\theta_{HCH} = 102.5°$ in the internal coordinates. In addition, there is a relatively larger barrier of 0.54 eV in the collinear abstraction channel. A lot of achievements have been made by the quantum mechanical (QM) and quasi-classical trajectory (QCT) methods [9-17]. based on the BHL PES. Later, Bãnares and co-workers constructed a new form of the $1^1A'$ PES using the Reproducing Kernel Hilbert Space (RKHS) interpolation method [18]. The new PES is free of spurious scale feature compared to the original BHL PES, and the dynamics of $C(^1D) + H_2$ and its isotope reactions have been studied by accurate close-coupled (CC) QM methods on the RKHS PES [19-23]. Also, a single sheeted double many-body expansion (DMBE) PES was reported by fitting accurate ab initio energies from the multireference configuration interaction method for the $1^1A'$ state of CH_2 [24], and the energies are corrected by the