REGULAR ARTICLE

An Investigation of Electronic Nonadiabaticity in the D + HBr and H + DBr Reaction on New Diabatic Potential Energy Surfaces

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Special Issue: Guo-Zhong He Festschrift

Abstract: Time-dependent wave packet calculations were carried out to investigate possible electronic nonadiabaticity in the D + HBr and H + DBr reactions on the new fitted diabatic potential energy surfaces by Han and coworkers [J. Chem. Phys., 137 (2012), 194305]. Reaction probabilities and integral cross sections are calculated. The results show negligible nonadiabatic effect for the title reactions in the energy range considered here, which is in accordance with the H + HBr and D + DBr reactions.

1 Introduction

The reactions of H + HBr [1-6] and Br + H$_2$ [7-10] are of fundamental importance in the development and understanding of elementary chemical kinetics and reaction dynamics, and play key roles in the hydrogen-bromine flame system [11]. The previous experimental investigations have been largely focused on the determination of reaction rates of the H + HBr abstraction and H + H'Br exchange reactions and kinetic isotope effects. However, due to the large mass of the Br atom and the very low barrier height of the H + HBr abstraction reaction (about 1.6 kcal/mol), it is a great challenge to accurately simulate multiple coupled

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potential energy surfaces for the BrH$_2$ system.

The approach of molecular hydrogen to an atom Br in a ^{2}P electronic state splits the degeneracy of this state, giving rise to three PESs [16]. Among them, two electronic states (1^2A' and 1^2A''; $^2\Sigma^+$ and $^2\Pi$ in linear geometry) correlate adiabatically with the ground-state atomic reactant Br(^{2}P$_{3/2}$) while a third state (2^2A'; $^2\Pi$ in linear geometry) correlates adiabatically with the excited-state atomic reactant Br(^{2}P$_{1/2}$) which is denoted by Br*. Of these, only the 1^2A' electronic state correlates with the electronic ground state of the products (HBr(X$^1\Sigma^+$) + H (^{2}S)). The PESs of the other states (1^2A'' and 2^2A') correlate with HBr products in the a$^3\Pi$ electronic state, which is considerably higher in energy [16]. Thus, if the Br + H$_2$ reaction were to proceed adiabatically on a single PES, as would be predicted by the Born-Oppenheimer (BO) approximation, then the excited SO state would not react. Based on the microscopic reversibility idea, the reaction H + HBr→Br* + H$_2$ (and other isotopic variants) would not occur at the presence of BO approximation. The excited Br* atom will be obtained mainly by means of nonadiabatic transition from ground PES to the excited PES via spin-orbit coupling element [14].

In the experimental aspects, inelastic and reactive scattering of Br*(^{2}P$_{1/2}$) with H$_2$ have been investigated by Nesbitt and Leone [12] by a systematic laser photolysis. They concluded that Br* + H$_2$ (v = 1) is efficiently quenched to Br + H$_2$ (v = 2) in the entrance channel, followed by subsequent H atom abstraction from vibrationally excited H$_2$. In 2005, Zare and co-workers [6] measured the rotational state distribution for the H + HBr→H$_2$ (v' = 2, j') +Br reaction at 53 kcal/mol collision energy and observed a small fraction of the H$_2$ molecule produced in highly rotationally excited states. Based on quasi-classical trajectory (QCT) calculations on a London-Eyring-Polanyi-Sato (LEPS) potential energy surface, they presented two distinct mechanisms: a direct reactive mechanism in which the trajectories stay near the collinear minimum energy path, and an indirect reactive mechanism in which the trajectories deviate significantly from the minimum energy path that are responsible for production of highly internally excited products. In order to determine the nonadiabatic effect in the H + HBr reaction, Zare and coworkers [13] performed an experiment on the D + DBr (v = 0) reaction by the ion imaging method over a wide set of collision energies. However, no detectable spin-orbit excited Br* atoms were found in their experiment, showing a very minor contribution of nonadiabatic channel for the D + DBr reaction. Therefore, they suggested that more experiments and calculations would be needed to understand how much the nonadiabatic transition affects this reaction. Recently, nonadiabatic dynamical calculations based on the new fitted diabatic potential energy surfaces by Han and coworkers [14] confirmed the experiment of Zare and coworkers.

On the theoretical side, many theoretical studies of both classical and quantum dynamics have been done for the BrH$_2$ system. Some years ago, Lynch et al. [15] constructed