Chemical Physics 381 (2011) 72–79

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Three-dimensional wave packet dynamics of $H_2 + D_2$ reaction

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ARTICLE INFO

Article history:
Received 10 September 2010
In final form 19 January 2011
Available online 4 February 2011

Keywords:
$H_2 + D_2$ reaction
Wave packet calculation

ABSTRACT

Initial state selected time-dependent wave packet calculations were carried out for the $H_2(v_1 = \text{high}) + D_2(v_2 = \text{low})$ reaction within a three degrees of freedom model. The probabilities for different competitive processes were studied on two realistic global potential energy surfaces (PESs) – BMKP and ASP. The orientation of the cold diatom did not greatly affect the reaction processes, while the orientation of the hot diatom had a significant effect. The BMKP surface generally gave lower energy thresholds than the ASP surface, except for the collision induced dissociation (CID) within the T_{II} geometry where the hot diatom comes in head-on perpendicular to the cold diatom. Isotopic substitution effects were studied on the recent BMKP PES. The $H_2 + D_2$ reaction was more effective for CID and showed more structured probability curves for single exchange reaction (SE) and three-body complex formation (3BC) than the $H_2 + H_2$ reaction.

1. Introduction

Exact quantum scattering calculations provide a complete description of the dynamics of a reaction and are thus the ultimate benchmarks for assessing various approximate theories and different models of reactivity [1,2]. Recent studies of chemical reaction dynamics in the gas phase have ranged from triatomic and tetratomic systems to larger polyatomic systems. In this regard, the mathematical representation of high-dimensional potential energy surface (PES) with chemical accuracy is a big challenge [3–6]. Collins and coworkers have developed an interpolation method to construct polyatomic molecular PESs [7,8]. Very recently, remarkable progress has been made by Bowman and coworkers who have implemented a different approach based on global fitting of *ab initio* electronic energies using a fitting basis that is manifestly invariant with respect to all permutations of like atoms [9,10]. The approach has been successfully applied to more than 20 complex molecules and clusters, such as CH_3CHO, CH_5^+, H_5^+ and water clusters [10]. Meanwhile, full-dimensional quantum scattering calculations for five- and six-atom reactions have been reported for $H_2 + C_2H$ [11], $H + NH_3$ [12], $H + CH_4$ [13–16] and $O + CH_4$ [17]. The recent dynamical calculations of six-atom molecular systems by combining efficient wave packet propagation (starting from the transition state of a reaction) with the multiconfiguration time-dependent Hartree (MCTDH) method have shown that the transition state based approach has computational advantages as well as providing an attractive conceptual interpretation [15].

The study of four-atom bimolecular reaction dynamics is of relevance in environmental chemistry and theoretically serves as a bridge between triatomic and polyatomic reactions [18]. Now, it is possible to carry out rigorous quantum scattering calculations on three- and four-atom reactions to provide rate constants and detailed state-to-state resolved information [19–29]. Zhang et al. [30] have performed a full-dimensional quantum mechanical study on the abstraction and exchange processes in the $H + H_2O$ reaction by treating both OH bonds in the H_2O reactant as reactive bonds. It suggested that one may be able to accurately study the four-center (4C) reaction which involves cleavage of two bonds $AB + CD \rightarrow AC + BD$, $AD + BC$, which is a special kind of four-atom reaction.

Four-center reactions have many novel dynamical features and thus have been widely studied both experimentally and theoretically in the past [31–35]. Unlike three-center reactions where only one bond is broken and formed during the reaction process, 4C reactions involve the simultaneous cleavage and formation of two bonds, and they usually present very high barriers, comparable to or higher than a covalent bond energy. Raz and Levine [32–35] have predicted (within a simple kinematic model) a strong kinematic constraint on the formation of products so that the effective energy threshold (dynamic threshold) for reaction becomes higher than the static barrier on the potential energy surface (energy threshold). The energy requirements and energy disposal in this kind of reaction are interesting subjects which have been considered by the same authors in a series of classical trajectory studies on 4C reactions induced by cluster impact. At the same time, the 4C process has to compete with two other reactions: collision

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doi:10.1016/j.chemphys.2011.01.012

induced dissociation (CID), AB + CD → A + B + CD, AB + C + D, which is known to be very important at the high energies where 4C reactions take place, and single exchange reaction (SE), AB + C-D → AC + B + D, AD + B + C, BC + A + D, BD + A + C. However, there are very few studies on 4C dynamics in a quantum framework. The coexistence of several processes and the higher energy required to surmount the barrier pose a challenge to the exact full-dimensional quantum studies of these processes. Therefore, most theoretical dynamics studies were based on classical or quasi-classical trajectories (QCT).

The $H_2 + H_2$ system is at the forefront of 4C collision dynamics. The study of the collisions between two hydrogen molecules is of particular interest in astrophysics [36], combustion [37,38] and spacecraft modeling [39]. Theoretically, the H_4 system is a fundamental system in quantum chemistry. Due to the light masses in the system, high level *ab initio* calculations are possible, and two global H_4 PESs have been reported: one by Aguado et al. (ASP) [40] and another by Boothroyd et al. (BMKP) [41]. As for dynamical studies, full-dimensional quantum–mechanical (QM) treatment of $H_2 + H_2$ is challenging due to the competition of several processes and the higher energy required. Hence, most theoretical studies have been performed using reduced dimensional quantum and (full-dimensional and reduced dimensional) QCT techniques. The first QM time-independent calculation using a reduced dimensionality approach, with one molecule in a highly vibrational excited state and another in the ground vibrational state, was carried out by Hernández and Clary [42]. The same model was subsequently investigated in greater detail and with higher accuracy by José Campos-Martínez et al. [43–46] and by Lu et al. [47] using wave packet propagation techniques. More recently, a comparison with the analogous reduced dimensionality QCT studies were reported [48]. Full-dimensional QCT studies of the dynamics of the $H_2 + H_2$ system and its isotopic variants have also been published in the last decade [49–56]. However, in the QCT approach, the absence of tunneling effects, which are expected to be important at threshold energies, and zero-point energy leakage can introduce significant errors. An important progress in the accurate calculations of the $H_2 + H_2$ reaction was made by Lu et al. [20], who obtained converged full-dimensional state-specific probabilities at the total angular momentum $\mathbf{J} = 0$. In their study, a comparison of three dimensional (3D) and six dimensional (6D) results showed reasonable agreement between them for the CID process. The scaled 3D probabilities (by a factor of 0.2) resembled the 6D results for the 4C process, except for an energy threshold shift of about 0.1 eV. These conclusions provide a central justification for the reduced 3D model employed in this paper. One of the aims of this paper is to study isotopic substitution effect, so the reduced three-dimensional wave packet dynamical results reported by Bartolomei et al. [45] have been used as a reference, and their results will be compared with those for the $H_2 + D_2$ reaction here.

Being one of the simplest diatom–diatom reactions, the mechanism of the exchange reaction between H_2 and D_2 is of interest. Here, we wish to understand the reaction mechanisms through more rigorous quantum dynamics simulation. We have extended the study from five restricted geometries of Bartolomei et al. [45] for $H_2 + H_2$ to six different geometries, as shown in Fig. 1. In contrast to Bartolomei et al.'s calculations which restricted all the reactants to be coplanar, three of our chosen geometries (H, X, X′) were studied for both coplanar and non-coplanar geometries in order to appraise the performance of the potential energy surfaces. These six geometries represent the main limiting geometries of the colliding system and will allow us to study all outcomes. The three geometries in Fig. 1 (H, X, T_I), with the more excited diatom perpendicular to the intermolecular distance *R*, are suitable for studying the effect of the orientation of the vibrational "colder" diatom in the reaction process. The geometry X′, with the lower excited diatom perpendicular to *R*, is suitable for studying the effect of the orientation of the "hotter" diatom. The remaining two geometries (T_{II}, L) with the more excited diatom parallel to *R*, have been chosen to investigate other products of the collision, such as SE product occurring for the L geometry and the formation of a three body complex (3BC), AB + CD → ACB + D, ADB + C, occurring for the T_{II} geometry. For all the processes, initial state selected probabilities for H_2 (initial vibrational state v_1 = high) + D_2(v_2 = low) have been computed. Our aim here is to investigate the different processes and related mechanisms occurring for each of the limiting geometries and to study isotopic substitution effects. The isotopic substitution effects were studied by comparing the CID, 4C, SE and 3BC probabilities for $H_2 + D_2$ reaction with the corresponding ones for $H_2 + H_2$ reaction reported by Bartolomei et al. [45]. Section 2 outlines the theoretical methodology of the initial state selected wave packet (ISSWP) method. In Section 3, results from dynamical calculations and comparisons of reaction probabilities for the two

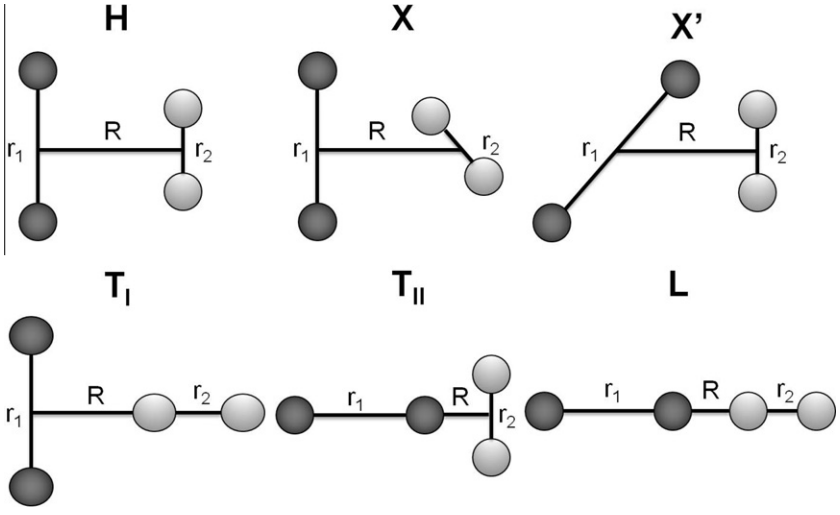

Fig. 1. Main coplanar configurations used in the reduced dimensionality calculations. For the parallel H geometry, both r_1 and r_2 are perpendicular to *R*. For the crossed X(X′) geometry, $r_1(r_2)$ is perpendicular to *R* and $r_2(r_1)$ has an angle of 45° with respect to *R*. $r_1(r_2)$ is perpendicular to *R* and r_2 (r_1) is parallel to *R* for the T-shaped T_I (T_{II}) geometry. The last L geometry is for the collinear case.