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Mechanism of the collision energy and reagent vibration's effects on the collision time for the reaction Ca + HCl

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ABSTRACT

The collision time which describes the speed of the collision process in a reaction is an important concept to an elementary chemical reaction. In this study, the quasiclassical trajectory method is applied to investigate the collision time of the reaction Ca + HCl ($\boldsymbol{v}$ = 0–2, $\boldsymbol{j}$ = 0) → CaCl + H. In order to provide a clear image of the reaction, the integral cross section we calculated is compared with corresponding quantum result and shows fairly good agreement. The results indicate that the collision energy and the initial vibrational level affect the average collision time remarkably. As the collision energy or the initial vibrational level increases, the average collision time decreases. The difference of average collision time for different initial vibrational level decreases with the increasing of collision energy. The product distributions as functions of scattering angle, attack angle and impact parameter are computed. Observing the functions, it can be found that the features could be caused by a competition among different parts of the product molecules with different collision time. For all the investigated initial vibrational levels, most of the reactive trajectories have the shorter collision times and are focused in several concentrated regions. Two possible mechanisms could be responsible for the HCl ($\boldsymbol{v}$ = 0) reaction in the concentrated regions. One is the sideway scattering and the system would fall into the deep potential well once in the collision process. The other is the weak forward scattering and strong backward scattering. The system would go around the deep potential well in the collision process. It is shown that the character of the weak forward scattering and strong backward scattering for the HCl ($\boldsymbol{v}$ = 1 and 2) reactions in the concentrated regions. However, the reactions outside the concentrated regions have the longer collision times and no particular mechanism. In the collision process, the system could fall into the deep potential well many times. We also explored the dynamics of the reaction at the same total energies but for different initial vibrational levels and found that the role of the insertion well becomes less and less important with the increasing of total energy.

1. Introduction

In past decades, chemical reactions between metal atoms and halide molecules have been the subject of theoretical and experimental studies. Generally the systems consisting of alkali (or alkali-earth) metal atoms (M) and hydrogen halides (HR, which R is a halide element such as F, Cl, Br or I) are the most representative prototypes of these reaction systems. These systems may be appropriate models to study the effects of collision energy and initial quantum state of the reagents on the reaction dynamics. These reactions are mainly dominated by the harpoon mechanism [1–3]. In the mechanism, one electron (or several electrons) of the metal atom "jumps" to the HR molecule and forms an anion. Then the anion splits to product molecule MR and H. Mestdagh et al. reviewed these reaction systems and gave a comprehensive description of them [1].

The molecular reaction dynamics for several hydrogen halides reacting with several alkali metal atoms (Li, Na) [2,4–7] and some reactions involving several alkali-earth metal atoms (Ca, Be, Sr, Mg, Ba) [8–19] have been theoretically and experimentally investigated. In the reactions with hydrogen halides, there is a similarity between alkali and alkali-earth metal atoms. The reaction process can be revealed as some crossings of potential curves between covalent states of the reagents and ionic states of the products [3,20]. Also, there is a vital difference between these two kinds of

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atoms [3,20]. An alkali metal atom has only one active electron, so one crossing is usually enough to understand the reaction process [21,22]. For an alkali-earth atom, it has more than one active electron. Thus, there are several crossing appearances which lead to multiple harpoon mechanisms (see Ref. [23] and the references therein). The reactive collision between alkali-earth metal atoms and hydrogen halides contains complicated variation in the electronic structure, which leads to various dynamics behaviors under different conditions. Moreover, the divalent nature of the alkali-earth metal atoms leads to a deep insertion well which corresponds to a collinear H–M–R complex. The deep well may be the main factor that contributes to the resonances with very long life time [20].

One of the widely studied systems in the reactions of an alkali-earth atom and a hydrogen halide is $Ca + HCl \rightarrow CaCl + H$, and many of the studies focused on the reactions with excited Ca atoms (see Ref. [3] and the references therein). The Ca (^1S) + HCl van der Waals complex had been studied experimentally [24–26] and the formation of the product CaCl was observed at particular electronic states [26]. It had been verified that the van der Waals complex Ca–HCl plays a vital role in the Ca + HCl reaction [24,27,28]. Moreover, Lawruszczuk et al. explained the importance of the ground electronic state of the system [26]. In this paper only the computational results of the ground state potential energy surface (PES) of the system were concerned. Theoretically, it is rather difficult to obtain sufficiently accurate PES for this system, because of the large amount of electrons in the system and complicated electronic structure change on the reaction path [3,20]. Before the accurate *ab initio* PES of the Ca + HCl reaction was reported by Verbockhaven et al. [3], there were only several PESs applied the diatomics-in-molecules (DIM) method [29,30]. In this work, all our reaction dynamics calculations are based on the PES of Verbockhaven et al. [3].

The PES developed by Verbockhaven et al. [3] is an accurate and full-dimensional PES of the Ca + HCl system on the ground state. It was obtained from a series of strict *ab initio* calculations at the multireference configuration-interaction (MRCI) level. The reaction Ca + HCl is endothermic by about 0.63 eV. Along the minimum energy reaction path, there is an energy barrier of about 0.55 eV. On both sides of the barrier, two energy wells appear at linear geometries. On the entrance channel it is a very shallow van der Waals well of about 0.024 eV, which is much smaller than the insertion potential energy well (about 2.09 eV) attributed to the linear $H^-Ca^{++}Cl^-$ configuration [3]. The reaction mechanism can be explained by the competition between the direct reaction which is dominated by the energy barrier and the indirect reaction which is attributed to the energy wells.

Theoretical studies about the Ca + HCl reaction's dynamics are quite scarce. Sanz et al. firstly studied this reaction for different initial quantum states of the HCl reagent using time-dependent wave-packet (TDWP) method, and they also simulated the infrared excitation from the Ca–HCl van der Waals well [20]. They found that the reaction is essentially direct, and there is no obvious change in the reaction efficiency as a function of the initial HCl quantum state. In addition, the reaction has an energy threshold at about 0.5 eV. Tang et al. studied the product polarization distribution of the Ca + HCl reaction at the collision energy of 20 kcal/mol, as well as the product ro-vibrational state distribution [31]. Wang et al. carried out a series of studies on the stereodynamics of the Ca + HCl reaction [32–34]. They have studied the effects of isotopic variant [32], vibrational excitation of the HCl reagent [33] and collision energy [34] on the stereodynamics of this reaction.

Although the aforementioned investigations fully covered the collisional dynamics and stereodynamics, we think it is interesting and necessary (or even inspiring) to explore how the reaction is shown on the dimensionality of time. The application of the concept of collision time [35] allows us to study the time evolution of the reaction process, as well as the speed of the reaction. In this work the collision time of the reaction are studied under different initial vibrational state of the reagent HCl and a wide range of collision energy (0.1–2.0 eV). The calculated collision time results are exhibited and discussed in detail related to different dynamics properties, including scattering angle, attack angle [36] and impact parameter. The paper is arranged as follows. In Section 2, we briefly introduce the methodology and computational details applied here, and all the results are presented and discussed in Section 3. In Section 4 we summarized the main conclusions of this work.

2. Theory and computation details

The QCT calculation method is basically the same as previous works [37–42]. Only some key details are presented here. The motions of the three atoms are simulated by a series of Hamilton's equations which are integrated with six order symplectic integration [43]. The collision energy E_c is chosen in the range of 0.1–2.0 eV, and the interval of two neighboring energies is 0.1 eV. The initial vibrational quantum number of reagent HCl is set as $\boldsymbol{v} = 0$–2. The initial rotational quantum number $\boldsymbol{j}$ is 0. At least 1.5×10^5 trajectories were run for each single condition (E_c, $\boldsymbol{v}$ and $\boldsymbol{j}$). The integration step size is chosen as 0.1 fs which guaranteed the calculated accuracy of the total energy and total angular momentum conservation better than 10^{-4} and 10^{-6}, respectively. The conservation is scaled by the equation $|V_i - V_f|/V_i$, where V_i and V_f are the initial and final values (total energy or total angular momentum), respectively. The initial distance from the atom Ca to the CM of the diatom HCl is set to 12 Å to ensure negligible initial interaction between them. The maximum impact parameters are properly set according to the initial condition of calculation.

The collision time τ_{col} is calculated by the following equation [35]:

$$\tau_{col} = \tau_{tot} - \frac{R_0 - R_{int}}{v_r} - \frac{R'_0 - R_{int}}{v'_r}. \tag{1}$$

τ_{tot} is the total duration time of a trajectory. R_0 and R'_0 are the initial and final atom–diatom distances, respectively. v_r and v'_r are the initial and final relative velocities, respectively. The truncation distance R_{int} is set to 4.2 Å. According to the definition, the collision starts at $R_0 = R_{int}$, and ends at $R'_0 = R_{int}$. Thus, the truncation distance R_{int} defines the boundary of the collision or interaction. The truncation distance is determined by carefully investigating the potential energy variation as a function of the reagent and product atom–diatom distances on the condition that all collision energies and initial vibrational levels are considered. In the frame of this definition the collision time is always greater than zero, even for the most direct trajectory. The definition shows that the collision time is also independent of initial and final states of the system. Hence, a common time concerning only the drastic interaction in the interaction region is allowed in all cases. The calculation process of the collision time applied in this work has been carefully tested and shows favorable numerical stability.

The average collision time τ_{avg} is calculated as

$$\tau_{avg} = \frac{\sum_{i=1}^{N_r} \tau_{col,i}}{N_r}, \tag{2}$$

where $\tau_{col,i}$ is the collision time of i th trajectory, and N_r is the number of reactive trajectories.

The final product distributions as functions of collision time, scattering angle, attack angle and impact parameter are reproduced by a fitting process using the method of moment expansion