

Theoretical Study on the Long-lived Complexes for the Na + I₂ Collision System

Xiao Min SUN, Da Cheng FENG, Zheng Ting CAI*

Institute of Theoretical Chemistry, Shandong University, Jinan 250100

Abstract: For the Na + I₂ collision system, theoretical study is performed on the QCISD(T) level by using *ab initio* method. The *ab initio* potential energy surfaces are got and on them the long-lived complexes are found and optimized. These results verify the crossed molecule beam experimental phenomenon and the detailed geometry structures are given for the first time. The role of the complexes in the reaction path is also described in detail.

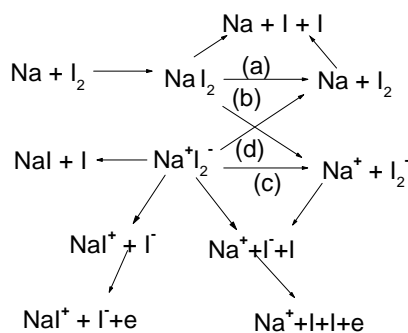
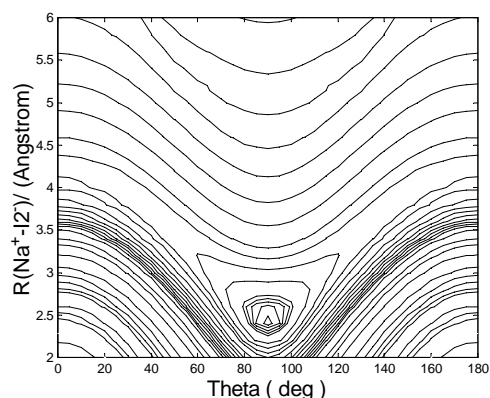
Keywords: Nonadiabatic transition, ion-pair formation, two-state potential energy surface, long-lived complex.

In the cross molecular beam experiments, the intensity contour maps observed for several ion-molecule reactions and atom-molecule reactions show a symmetry about $\theta=90^\circ$. The symmetric feature reflects the existence of a long-lived complex, so that before the reaction is completed, this complex may rotate several turns and lose all memory of the original direction of the colliding particles.

For the titled system, the previous potential energy surface studies are mainly as follows: Aten et al. have developed a semiempirical PES¹. Recently Feng et al.² have reported the first *ab initio* PES and Cai et al.³ conducted the theoretical study of the scattering resonance state for the titled system. In this paper, the detailed study on ion-pair formation and reactive process for the Na+I₂ collision system is performed on the QCISD(T) level. The *ab initio* potential energy surfaces are got and on them the long-lived complexes are found and optimized. These results verify the crossed molecule beam experimental phenomenon and the detailed geometry structures are given for the first time. The modified mechanism is proposed in which the role of collision complex is mainly considered.

The reaction coordinate is illustrated in Ref. 2, and the main channels are listed in **Figure 1**. Firstly, the collision between ionic state and covalent state is investigated from various angles with the fixed distance of I₂ molecule. The PESs dependent on angle θ of the ionic and covalent state are shown in **Figure 2** and **Figure 3**. It is worth noting that electronic states and symmetries of the ionic and covalent state vary with different angle θ . With equal symmetry and multiplicity the covalent and ionic states are avoided. Only under the condition of $\theta=90^\circ$, the two-state PESs cross, *i.e.*, the electronic motion couples

* E-mail: zhtcai@sdu.edu.cn

Figure 1 The possible channels for Na+I₂ collision system**Figure 2** The ionic collision PES with angle θ ranging from 0° to 180°

with translation, rotation and vibration of the system.

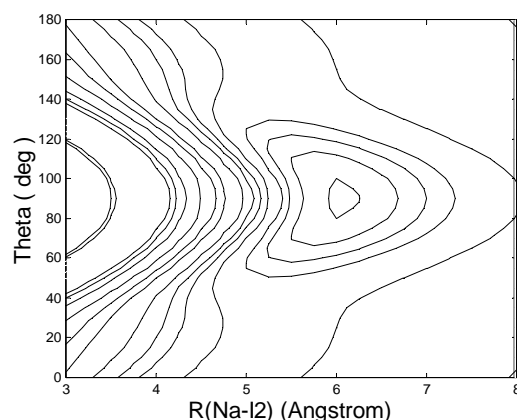
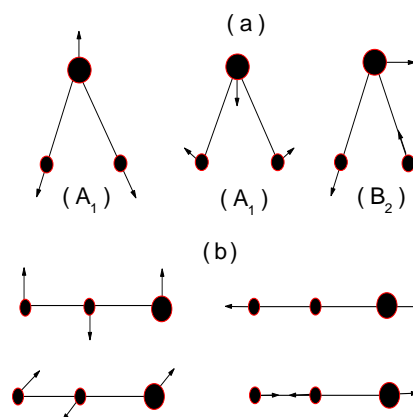
On the ionic state PES (seen in **Figure 2**), as R increases with fixed angle θ or as θ increases with fixed R , energies of the collision system are decrease first and then increase, thus a basin appears and a stable complex is formed. Through the same analysis, the other complex is found on the covalent PES (seen in **Figure 3**). From the above analysis, the long-lived complex is formed under the case of $\theta=90^\circ$, *i.e.*, T-type collision, and the electron is evenly distributed on two I atoms in the process of ion-pair formation. Hence, T-type collision is a very important case in the study of ion-pair formation.

The optimized results of geometry structures are given in **Table 1**, where numerical gradients are used to optimize the reactant, long-lived complex and product, meanwhile, the vibration analysis and zero-energy correction are carried out on the stable points. Configuration A, B and C correspond to the minimum energy points on 2A_1 , 2B_2 and ${}^2\Sigma$ state PES respectively.

Configuration A is a van der Waals complex in the very smooth and shallow potential valley of 2A_1 state PES, whose frequencies are 1.35 (A_1) cm^{-1} , 12.40 (B_2) cm^{-1} , 156.81 (A_1) cm^{-1} . From the natural bond orbital (NBO) population analysis on the QCISD level, it is known that the net charge on each atom is nearly zero. Similarly, the configuration B is a long-time complex in the deep potential valley of 2B_2 state PES whose frequencies are 83.75 (B_2) cm^{-1} , 160.25 (A_1) cm^{-1} , 217.03 (A_1) cm^{-1} . The population analysis illustrates that this complex is a strong polar intermediate (the net charge on Na and each I is +0.9147 and -0.4573, respectively). The vibration analysis is shown in **Figure 4**. The vibration models of configuration A and B are the same as those of H₂O.

Table 1 The geometry optimized results of the reactant, the product and collision complex

| Sample | $\theta(^{\circ})$ | R (nm) | r_1 (nm) | r_2 (nm) | E_{tot} (a.u.) |
|--|--------------------|----------|------------|------------|-------------------------|
| Na + I ₂ | / | ∞ | 0.292 | / | -184.2485 |
| Na ⁺ + I ₂ ⁻ | / | ∞ | 0.346 | / | -184.1627 |
| NaI + I | / | ∞ | ∞ | 0.272 | -184.3258 |
| Na I ₂ (2A_1 state) | 90 | 0.292 | 0.548 | / | -184.2493 |
| Na ⁺ I ₂ ⁻ (2B_2 state) | 90 | 0.354 | 0.226 | / | -184.3505 |
| NaII (${}^2\Sigma$ state) | 180 | 0.463 | 0.382 | 0.272 | -184.3298 |

Figure 3 The covalent collision PES with angle θ ranging from 0° to 180° **Figure 4** The vibrational frequency analysis of the long-lived complex (a) T-type case, (b) collinear case.

As for configuration C, it lies at the potential valley of 2Σ state PES. It is interesting that configuration C has two virtual frequencies and another two frequencies are real. The concrete values are -17.07 (Π) cm^{-1} , -17.04 (Π) cm^{-1} , 36.33 (Σ) cm^{-1} , 257.45 (Σ) cm^{-1} , respectively. It is well known that the collinear tri-atom system has four degrees of freedom in terms of the expression of $3n-5$ (n , the number of the atoms). The reliable interpretation for the two virtual frequencies is that: supposing the collinear tri-atom lies on X axis (the detailed coordinate is shown in **Figure 5**), configuration C corresponds to the minimum energy point when Na atom approaches to the I_2 molecule along X axis. However, as illustrated in the case of (a), when Na atom approaches to the I_2 along every line on XOY plane, the energy of the counterpart of configuration C decreases, that is to say, configuration C is the saddle point along the minimum energy path (MEP) on XOY plane. Similarly, configuration C is the saddle point along the MEP on XOZ plane, too. So configuration C is the so-called second-order saddle point. It is obvious that the two cases are equal to each other, which lead to the nearly equal frequency.

The T-type collision potential curves are drawn in **Figure 6** in order to illustrate the detailed process of ion-pair formation. From **Figure 6**, it can be known that the whole ion-pair formation process, *i.e.*, the reaction path, can be described as follows: while Na atom approaches to I_2 molecule along the $2A_1$ state PES, the potential energy mildly decreases, firstly, it till reaches the bottom of the first potential well, where the van der Waals configuration A is formed, and then the potential energy increased gradually and stabilized. At $R_c \approx 0.493$ nm, the $2A_1$ state PES crosses with $2B_2$ state PES, where there are two optional paths. Path one is moving continuously on the $2A_1$ state PES. The other is jumped to $2B_2$ state PES, the electron transfers and Na^+ and I_2^- are formed. Under the effect of strong Coulomb force between Na^+ and I_2^- , the potential energy drops sharply, when Na^+ continues to approach to I_2^- molecule anion and reaches the bottom of the second well, the strong polar complex B appears. After Na^+ departs from I_2^- , ionizing collision is completed. Clearly, there are two interaction paths leading to ionization. The first interaction path is called covalent scattering (**Figure 5**). In this case the first

crossing is passed adiabatically (process a) and the second one is passed diabatically (process b); the transition to the ionic state takes place at the second crossing. The larger part of the trajectory is located on the covalent potential surface. The second interaction path is called ionic scattering. Here the first crossing is passed diabatically (process c) and the second one is passed adiabatically (process d); the transition to the ionic state occurs at the first crossing. It should be noted that the van der Waals collision complex forms firstly and then it crosses between the covalent and ionic state PES, so that the double-potential well structure is found, though one of them is very shallow. The result is similar to Marcus' electronic transfer theory^{4,5}.

Figure 5 The relative motion between Na atom and I₂ molecule from the collinear configuration to the T-type configuration.

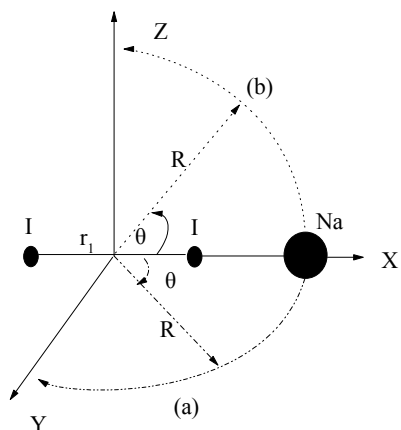
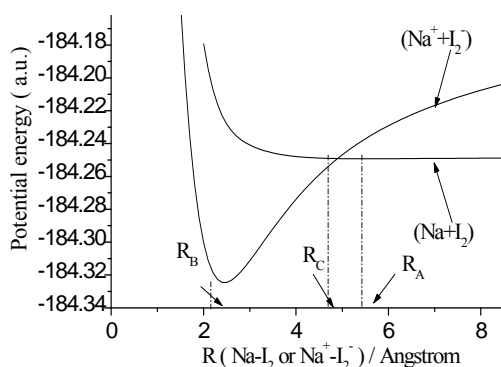


Figure 6 The crossing potential curves of the two-state PESs under the T-type case.



In summary, a detailed mechanism for ion-pair formation is proposed which mainly considers the role of collision complex in reaction path. It is helpful for guiding the experiments

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