An *Ab initio* Theoretical Study on the Nonadiabatic Coupling for $Na + I_2$ Collision System

SUN, Xiao-Min(孙孝敏) **CAI, Zheng-Ting***(蔡政亭) **FENG, Da-Cheng**(冯大诚)
Institute of Theoretical Chemistry, Shandong University, Jinan, Shandong 250100, China

The ionic and neutral state potential energy surfaces (PESs) of $Na + I_2$ collision system have been calculated on QCISD(T) level by using *ab initio* method. The location and depth of the potential well, the collision radius and their fine structures have been analyzed at the equilibrium geometry of I_2 molecule. The electronic transfer probabilities are also calculated in terms of Landau-Zener model. The lifetime of scattering resonance state is evaluated by the uncertainty principle. All the results have been compared with those obtained according to the Aten-Lanting-Los PES and Feng's PES.

Keywords *ab initio*, ion-pair formation process, potential energy surface nonadiabatic coupling, scattering resonance state

Introduction

Ion-pair formation process is a very important kind of chemical reactions, which has significant theoretical and experimental values in revealing the mechanism of microscopic reaction dynamics. The potential energy surface (PES) is capable of providing the information necessary for microscopic reaction dynamics. The $Na + I_2$ collision system is a typical ion-pair formation process. However, this kind of reaction involves the non-adiabatic coupling of two states (ionic state and neutral one), which results in difficulties to chemists.

So far, for $Na + I_2$ collision system, Aten *et al*.[1] have developed a semiempirical PES and Ma *et al*.[2a,2b] have performed the collinear reaction probabilities on it using extended LCAC-SW (linear combination of arrangement channels-scattering wavefunction) quantum scattering dynamic method. Banares *et al*.[3] studied its differential reaction section by laser-crossed beam experiment. Recently Feng *et al*.[4] have reported the first *ab initio* PES and Cai *et al*.[5] perform the theoretical study of the scattering resonance state for the titled system. In the previous work, it should be noted that the negative charge is distributed evenly over the two halogen atoms during the interaction in one of the basic hypotheses of Aten-Lanting-Los PES, which is absolutely the case only under the *T*-type collision; while in other cases, especially under the collinear collision, the negative charge almost concentrates on one halogen atom. Feng *et al*.[4] adopted smaller basis sets in constructing their PESs. Thus, by calculation and comparison, larger basis sets are adopted in this paper and more attention is paid to the *T*-type collision, too.

Calculation methods

In the present paper the ionic and neutral state PESs of $Na + I_2$ collision system have been reconstructed on QCISD(T)[6] level with larger basis sets (6-311 + G* basis set is used for Na atom, SDD[7] basis set includes relativistic effect for I atom). Meanwhile, the nonadiabatic coupling region between two states PESs has been analyzed. The electronic transfer probabilities were also calculated in terms of Landau-Zener model.[8]

Results and discussion

The results are compared with those obtained according to the Aten-Lanting-Los (ALL) PES and Feng's PES[4]. The reaction coordinate is illustrated in Fig. 1, where R represents the distance between Na atom and the mass center of I_2 molecule, r_1 the diameter of I_2 molecule. The *T*-type ($\theta = 90°$) structure with C_{2v} symmetry is mainly considered. The structure has two different electronic states, *i.e.*, neutral state ($^2A_1$) and ionic state ($^2B_2$). The results of different potential curves (PCs) are shown in Table 1. The whole PESs of two states are illustrated in Figs. 2 and 3, in which Fig. 2 is the neutral state PES including two cases, one is the three dimensional (3D) PES, and the other is the contour of 3D PES; of Fig. 3 corresponding to ionic state one, the detailed titles are the same as those in Fig. 2. Potential curves (PCs) are demonstrated in Fig. 4. In them, Fig. 4(a) is got in accordance with Aten-Lanting-Los PES. Fig. 4(b) is the results of Feng's PES. Fig. 4(c) is the new result. In Fig. 5, the electronic distribution of the fine structure is presented. The electronic transfer probabilities are provided in Fig. 6 accord-

* E-mail: zhtcai@sdu.edu.cn; Fax: 0531-8564464; Tel.: 0531-8365748
Received October 22, 2002; revised January 18, 2003; accepted February 25, 2003.
Project supported by the National Natural Science Foundation of China (No. 20173032) and the Ph.D. Special Research Foundation of Chinese Education Department.

ing to Landau-Zener model.

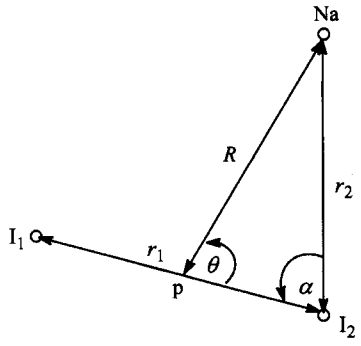

Fig. 1 Reaction coordinate (p represents the center of I_2 molecule).

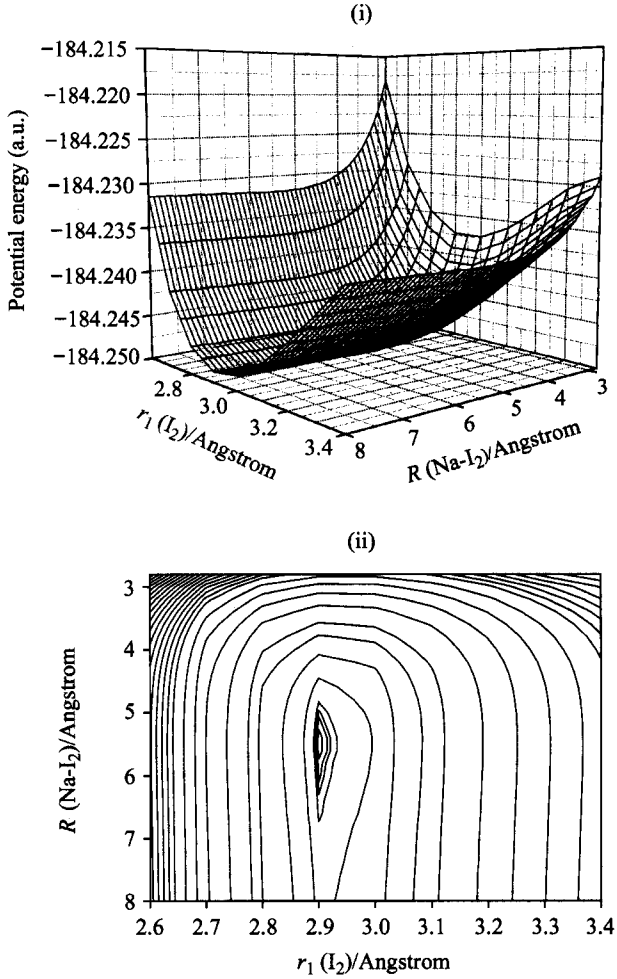

Fig. 2 Neutral state PES for $Na + I_2 \rightarrow Na + I_2$ *T*-type collision system. (i) the 3D PES; (ii) the contour of 3D PES. r_1 (I_2) represents the diameter of I_2 molecule; *R* (Na-I_2) represents the distance between the Na atom and the mass center of I_2 molecule.

From Table 1, Figs. 2—6, we can see that:

(1) In Figs. 2 and 3, the whole PESs are calculated with the scanning for r_1 and *R* with the step-length 0.01 nm and 0.02 nm respectively. The equal-counter potential plots are shown in Fig. 2 for $^2A_1$ state and Fig. 3 for $^2B_2$

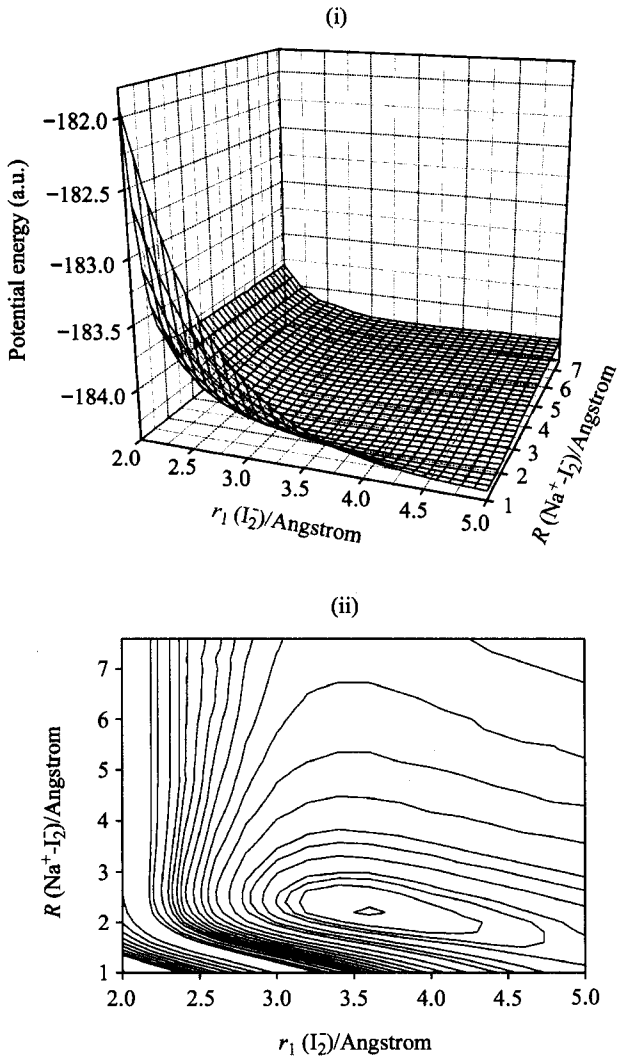

Fig. 3 Ionic state PES for $Na + I_2 \rightarrow Na^+ + I_2^-$ *T*-type collision system. (i) the 3D PES; (ii) the contour of 3D PES. r_1 (I_2^-) represents the diameter of I_2^- molecule anion; R (Na^+-I_2^-) represents the distance between the Na^+ cation and the mass center of I_2^- molecule anion.

state. The minimum energy reaction pathway on the $^2A_1$ state and $^2B_2$ state can be found on Figs. 2 and 3, respectively. It is obvious that two PESs are crossed. At the crossed point the harpoon process of the electron leaping occurs. It should be pointed out that each geometric structure on ionic state PES is strong polar and the positive charge is almost centered on Na atom, while on neutral state PES every geometric structure is neutral and the net electric charges either in Na atom or in I atom are almost zero, and it is confirmed by the calculation of electronic distribution.

(2) To $^2A_1$ state, there is a very shallow and smooth potential well on both *ab initio* (including Feng's result and this paper's) and Aten-Lanting-Los potential curve. The results obtained from *ab initio* calculation indicate that the structure here (in the corresponding coordination, r_1 = 0.2924 nm and R = 0.5473 nm) is very loose and that Van der Waals complex is formed, whose frequency (B_2,

Table 1 Results comparison of different PCs

PCs	R_c[a] (nm)	$R_{min(con)}$[b] (nm)	ΔE_{con}[c] (eV)	$R_{min(ion)}$[d] (nm)	ΔE_{ion}[e] (eV)
ALL	0.5470	0.2625	0.04000	0.1995	4.1305
Feng's	0.4759	0.5371	0.01415	0.2678	3.3821
This paper's	0.4896	0.5473	0.01551	0.2452	3.5484

[a] The compact radius between the convelant and ionic states (obtained step by step); [b] the distance corresponding to the minimum energy on the neutral state potential curve; [c] the depth of the potential well on the neutral state potential curve; [d] the distance corresponding to the minimum energy on ionic state potential curve; [e] the depth of the potential well on the ionic state potential curve.

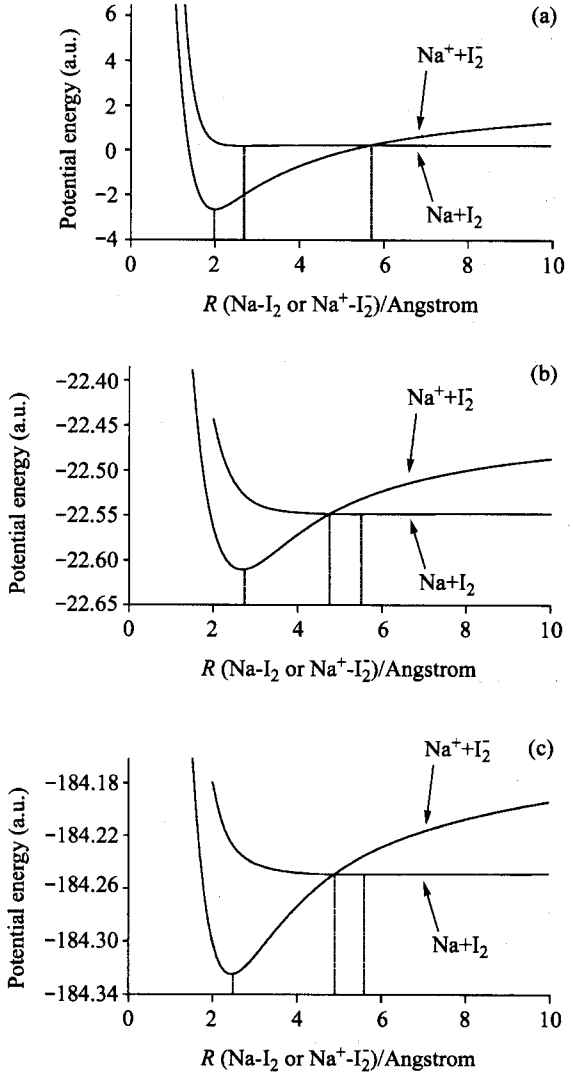

Fig. 4 Comparison of different potential curves (PCs) (during calculation, r_1 is frozen at 0.2924 nm). (a) ALL; (b) Feng's PCs; (c) this paper's PCs.

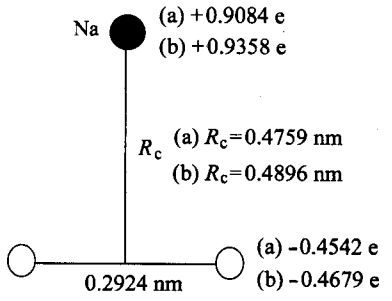

Fig. 5 Electronic structure at compact radius (R_c). (a) Feng's method; (b) this paper's.

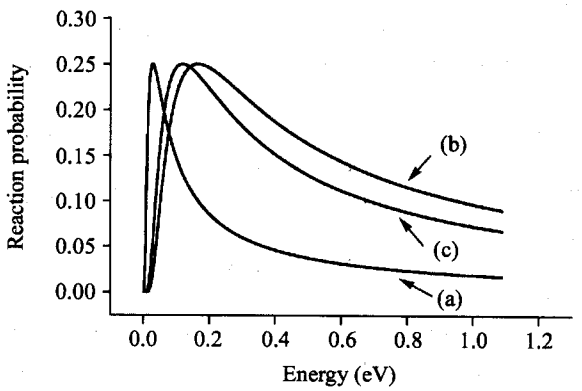

Fig. 6 Electronic transfer probability between two states according to Landau-Zener model. (a) Aten-Lanting-Los result; (b) Feng's result; (c) this paper's result.

2.3244 cm^{-1}; A_1, 12.4294 cm^{-1}; A_1, 156.3393 cm^{-1}) shows that it is unstable. The frequency illustrates that this geometry structure lies in not only the lowest energy point on the potential curve but also the minimum energy reaction path.

(3) While to $^2B_2$ state, a very deep potential well exists on both curves mentioned above. Its tight structure demonstrates that a long-life complex in which r_1 and R are 0.2924 nm and 0.2452 nm respectively comes into being. The frequency of this complex is 144.4417 cm^{-1} (B_2), 202.5315 cm^{-1} (A_1), 241.9580 cm^{-1} (A_1) and shows its stability.

(4) The quite large compact radius (R_c) may lead to a very large reaction section (πR_c^2) according to harpoon mechanism.[8] To calculate according to the Aten-Lanting-los PES, Feng's PES and this paper's PES in turn, the reaction section is 0.9401 nm^2, 0.7114 nm^2, 0.7531 nm^2 respectively, and all these results are qualitatively in agreement with the Laser-crossed molecular beam experiment[9] and the semi-empirical calculation[10] whose concrete values are 0.97 nm^2 and 0.66 nm^2, respectively. The electronic analysis of the structure is illustrated in Fig. 5. The electric transition easily occurs from neutral state to ionic state and at this moment above 90% of the electron transfers from Na atom to I_2 molecule.

(5) It is a common feature to form the probability peak which indicates the typical energy resonance, but each one is different from another. The probability peak calculated from Aten-Lanting-Los PESs is narrow and

comes into being earlier, while the one of Feng's is broad and is formed later. Our result is between them. It is clearly illustrated in Fig. 6. In the case of (a), the narrow probability peak implies that the lifetime of resonance state is short. Under the conditions of (b) and (c), the broad peaks correspond to the long lifetime of resonance state. The broader the probability peak is, the longer the lifetime of resonance state. According to uncertainty principle, the resonance state lifetime of the electronic transfer process is about 10^{-14}—10^{-13} second, which is calculated from the above three PESs and qualitatively in agreement with the normal experimental result. In fact, the electronic transfer process is controlled by the width of nonadiabatic coupling region and the gap between the neutral and ionic state PES.

Conclusions

On the basis of above analyses the conclusions are as follows:

(1) The *T*-type collision potential curves of Na + I_2 (neutral state) and $Na^+ + I_2^-$ (ionic state) are crossing, which is in agreement with the Aten-Lanting-Los potential ones. But the crossing points obtained with the abovethree methods are different. This is easy to understand because the Aten-Lanting-Los PES is semi-empirical and reliable only qualitatively and semi-quantitatively. In addition, the collinear collision potential curves of two above states are crossing nonadiabaticlly too.[1] The two potential curves of Na + Cl and $Na^+ + Cl^-$ or Na + I and $Na^+ + I^-$ avoid crossing.[11]

(2) For $Na + I_2 \rightarrow Na^+ + I_2^-$, above 90% of electrons have been transmitted on the nonadiabatic coupling point (R_c) of the two state PESs. The transitional process is extremely swift and completes in a femto second according to Cai's study.[5,12]

(3) In the present paper, for the first time, the electronic transfer probability using the *ab initio* PES and the fine structure at the crossing point are reported. These data are of great value for the study on the formation mechanism of the scattering resonance state for $Na + I_2 \rightarrow Na^+ + I_2^-$ reaction. From the above, the physical picture of ion-pair formation process, *i.e.*, the electronic transition process is described in detail. The picture and data provided in this paper lay a solid foundation for further studying the reaction dynamics and scattering resonance state of $Na + I_2 \rightarrow Na^+ + I_2^-$ reaction.

References

1 Aten, J. A.; Lanting, G. E. H.; Los, J. *Chem. Phys.* **1977**, *19*, 241.

2 (a) Ma, W.-Y.; Cai, Z.-T.; Deng, C.-H. *Chem. Phys. Lett.* **1999**, *304*, 117.
(b) Ma, W.-Y.; Cai, Z.-T.; Deng, C.-H. *Chem. Phys. Lett.* **1998**, *10*, 325.

3 Banares, L.; Velarde, M. G.; Urena, A. G. *J. Chem. Phys.* **1991**, *95*, 5474.

4 Feng, D.-C.; Kang, C.-M.; Qi, C.-S.; Cai, Z.-T. *Chem. Phys. Lett.* **2002**, *355*, 285.

5 Cai, Z.-T.; Ma, W.-Y.; Sun, X.-M.; Feng, D.-C. *Chem. J. Chin. Univ.* **2002**, *23*, 1776 (in Chinese).

6 Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

7 Fuenteala, P.; Preuss, H.; Stoll, H.; Szentpaly, L. V. *Chem. Phys. Lett.* **1982**, *89*, 418.

8 Erying, H.; Lin, S. H.; Lin, S. M. *Basic Chemical Kinetics*, John Wiley & sons, **1980**, pp. 243—245.

9 Edelstein, S. A.; Davidovits, P. *J. Chem. Phys.* **1971**, *55*, 5164.

10 Anderson, R. W.; Herschbach, D. R. *J. Chem. Phys.* **1975**, *62*, 2666.

11 Guest, M. F.; Hirst, D. M. *Chem. Phys. Lett.* **1981**, *84*, 167.

12 Cai, Z.-T.; Ma, W.-Y.; Sun, X.-M.; Feng, D.-C. In *Abstract Book of Second Worldwise Chinese Theoretical and Computational Chemistry Conference*, Taipei, **2002**, *9*, p. 14.

(E0210222 ZHAO, X. J.; FAN, Y. Y.)