The Quantum Scattering Study for Ion-pair Formation Reaction Na+I$_2$→Na$^+$+I$_2^-$ with the LCAC-SW method

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Abstract: The selected-state probabilities of collinear ion-pair formation process Na+I$_2$→Na$^+$+I$_2^-$ on Aten-Lanting-Los two-state potential energy surface have been calculated by using LCAC-SW method. The results show that reaction probabilities are oscillatory with collision energy; the threshold energy of this ionization reaction is 2.8 ev, which is in modest agreement with experimental result.

Keywords: Ion-pair formation, reaction probability, quantum scattering, LCAC-SW method.

Ion-pair formation process is a kind of very important chemical reactions whose theoretical and experimental studies are significant to the revealing of the microscopic dynamics of gas-phase, liquid-phase reactions and upper-space atmosphere reactions. This kind of reactions concerns two electronic state PESs (potential energy surfaces) and their crossing effect, so the theoretical treatment is very complicated. It has been reported that perturbation method, classical trajectory surface-hopping model and Miller's S-matrix variation method had been proposed of which each had its own satisfactory points, but also had some shortcomings.

C. H. Deng constructed a new quantum scattering method called the linear combination of arrangement channels-scattering wavefunction (LCAC-SW) approach[1], with which we have calculated the collinear reaction probabilities of F+H$_2$→HF+H system[2], the results are satisfying. In this paper, LCAC-SW approach has been extended to the ion-pair formation process, the selected-state probabilities of collinear reaction Na+I$_2$→Na$^+$+I$_2^-$ on Alen-Lanting-Los[3] two-state PESs have been calculated with the extended LCAC-SW method which can be seen in the next paper[4]. The results are displayed in **Figure 1**.

From **Figure 1** we can see that: (1) the reaction threshold energy is 2.8 ev, which is in modest agreement with experimental result 2.6±0.1 ev[5]; (2) these sharp peaks denote the strong resonance of the reaction probabilities. The transfer of electron moving back and forth has high frequencies, the process being based on the widths of covalence-state PES and ionic-state PES and the crevice between the two state PESs. The resonance of reaction probabilities have been observed for a lot of heavy-light-heavy reactive systems

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Figure 1 The selected-state probabilities for $Na+I_2(v) \rightarrow Na^+ + I_2^-$ (a,v=0; b,v=1)

a   b
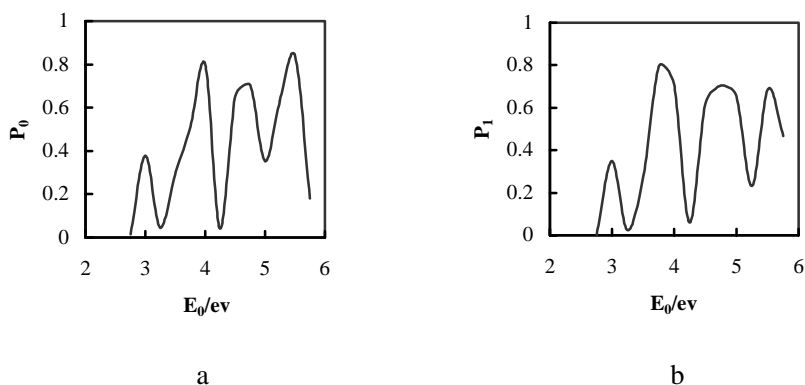
(for example, $I+HI \rightarrow IH+I$[6]). For the $Na+I_2 \rightarrow Na^+ + I_2^-$ system, the transferred electron is much lighter than hydrogen atom, so the resonance behavior is also much stronger. A new viewpoint of theoretical dynamics suggests that "dynamic valley"[7] may appear in some collision processes of chemical reaction. The "dynamic valley" is not the same as the "intrinsic valley" on reaction PES. The former is concerned with the formation of complex-state, but the latter is concerned with the formation of long life-time complex and has nothing to do with collision energy. There is no intrinsic valley on PESs of $Na+I_2 \rightarrow Na^+ + I_2^-$ system, so it seems that the resonance behavior of probabilities of ion-pair formation is related to "dynamic valley". The formation of "dynamic valley" is related to interference effect of states (translational state-internal state; states of reactant-states of product) of reaction system.

Acknowledgments

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