§14. Quantum Mechanical Study of Collinear Reactive and Dissociative He + H_2^+ Collisions

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We have developed the numerical method[1] to investigate chemical reaction and dissociation processes in atom-diatom collisions. We have numerically tested by applying this method to He + $H_2^+(v) \rightarrow HeH^+(v')$ + H collinear rearrangement collision.[2] Here, the total energy of the collision system is increased above the dissociation threshold of H_2^+, and we have investigated the energy dependence of the dissociation process He + $H_2^+(v) \rightarrow$ He + H + H^+ and of the reaction He + $H_2^+(v) \rightarrow HeH^+(v')$ + H over a range of the total energy from 2.2 to 10 eV. We have employed an accurate potential energy surface provided by Joseph and Sathyamurthy.[3]

Many resonances are revealed in vibrationally inelastic and reaction channels at the total energy below the dissociation threshold. Some of these resonances are identified as those of closed channels, that is, the Feshbach type, and the others are of open channels. Since our main subject in this paper is the energy dependence of reaction and dissociation processes, we do not pursue further resonance phenomena.

Probabilities of vibrationally inelastic scatterings become smaller without any exception for the initial vibrational state as the total energy is increased from the dissociation threshold to 10 eV. That is, the collision always proceeds to an atom rearrangement or a dissociative process.

If the initial vibrational state is below v = 4, the probability of dissociation process is very small, that is, the collision almost always ends up with a formation of HeH^+, even if the total energy is increased up to 10 eV. On the other hand, if the initial vibrational state is above v = 11 - 13 depending on the total energy, the dissociation of the H_2^+ ion becomes the main process. For these two extreme cases, the energy dependence of both probabilities of reaction and dissociation is very weak. These results show that a coupling between the reaction and dissociation channels is not so strong as we supposed.

For the initial vibrational states between 5 and (10-12) depending on the total energy, the magnitude of exchange reaction probability is comparable with the one of dissociation probability. In these cases, rearrangement and dissociation processes compete with each other through the formation of both arrangements HeH^+H, which preferentially leads to the rearrangement, and $HeHH,^+$ which becomes inevitably to the dissociation during the collision. Therefore, both probabilities of rearrangement and dissociation depend on the total energy as being expected and show undulatory behavior as a function of the total energy.

We have obtained the interested results on the energy dependence of the reaction probability. The vibrational distribution of the product HeH^+ ion is strongly correlated with the one of the initial H_2^+ ion. This interesting correlation persists in a wide range of the total energy between 4 - 10 eV.

A detailed description of our method, further details on these findings, and a full discussion shall be published.[4]

References

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