Reaction dynamics of ion-molecule collision beyond reaction-path-based understanding

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The automated reaction path search methods enable us to construct the network of an enormous number of reaction paths over a vast potential energy surface of a molecular system.[1] The guided ion beam experiment can obtain all the relative formation energies of product ions in ion-molecule collision reactions. These two techniques were supposed to give consistent information. However, the experiment on the CF_3^+/CO system showed much higher formation energy for CF^+ ion (7.48±0.15 eV) than the theoretical prediction (2.30 eV), suggesting that the experimental molecular system ignored reaction paths leading to the CF^+/F_2CO channel (**Fig. 1**).[2] Although this inconsistency necessitated further investigations of reaction dynamics, it was difficult to simulate this reaction due to a small reaction cross section. In this study, we carried out on-the-fly molecular dynamics (MD) simulations with appropriate initial conditions that efficiently cause chemical reactions and revealed the reaction dynamics far different from the reaction-path-based understanding.

In bimolecular reactions with high translational energy, on-the-fly MD studies have demonstrated that reactants directly reach a transition state without forming a pre-reaction complex.[3] For such a direct reaction, there seems to be an optimal relative orientation of reactants to cross a transition state efficiently.[4] We prepared initial conditions for collisional simulations based on the optimal situation and obtained reactive trajectories, which smoothly reached the FCO^+/CF_2 channel. The MD simulations indicate that the molecular systems which cross a transition state have significantly limited relative orientations and atomic-momentum directions, resulting in the ignorance of reaction paths in the experiment.

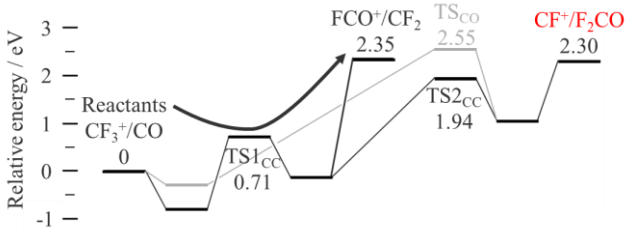

Fig. 1. Two series of reaction paths (black or gray lines) leading to CF^+/F_2CO (red) and schematical reaction dynamics (black arrow) reaching FCO^+/CF_2.

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