

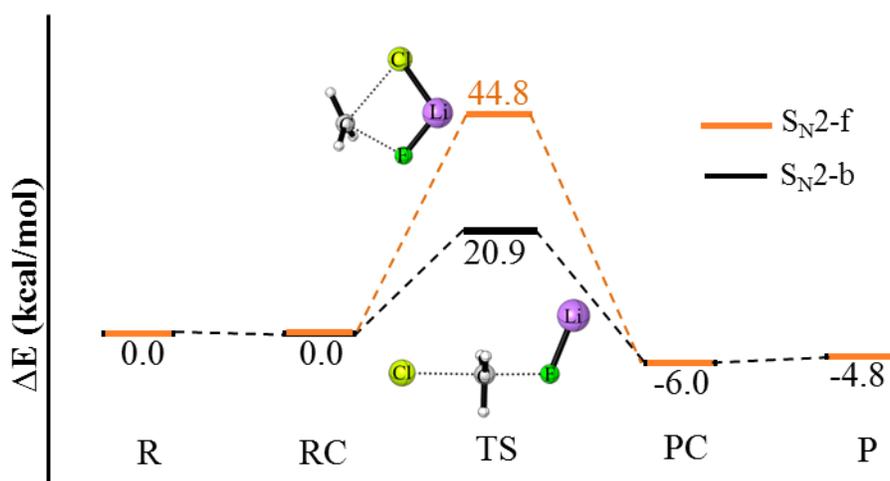
## Theoretical Study of Ion Pair S<sub>N</sub>2 Reactions

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Bimolecular nucleophilic substitution (S<sub>N</sub>2) reaction is one of the fundamental types of chemical reactions and plays a significant role in organic, inorganic and biological reactions. Theoretical investigations have been instrumental in complementing experimental ones over several decades of intensive study. Interestingly, new findings are still being made, especially, in terms of the reaction mechanisms. Ion pair nucleophiles, often the source of the bare nucleophiles, have received less attention in the study of non-identity S<sub>N</sub>2 reactions. The effect of aprotic solvents also necessitates further study. The fluoride anion, in the presence of metal cations, prefers the frontside attack. This is important for fluorine substitution and the stereochemistry of the products. The reactions of MF + CH<sub>3</sub>Cl (M = Li, Na and MgCl) have been studied for the frontside and backside attacks in the gas phase and aprotic THF solvent using the OLYP functional. The intrinsic reaction coordinates computations have been analysed in details using the activation strain model, which has been extended to include solvation effects. When a non-cyclic TS was located in the backside reaction (Figure 1), the latter reaction was favoured rather than the frontside one. In the gas phase, the reaction involving the ion pair nucleophile NaF did not show a cyclic TS. As the charge density of the cation increases, the tendency to form a cyclic TS increases and the preference for the frontside reaction increases. The additional stability provided by THF prevents the formation of a cyclic TS for reactions involving ion pair nucleophiles NaF and LiF in THF. The activation strain analysis sheds light on the difficulty in forming the cyclic TS and highlights the stabilizing effect of THF. This work pioneers the use of the activation strain model in the study of ion pair S<sub>N</sub>2 reactions.



**Figure 1:** Backside (S<sub>N</sub>2-b) versus frontside (S<sub>N</sub>2-f) reaction profiles for ion pair nucleophile LiF in THF, computed at (PCM) OLYP, showing cyclic TS for S<sub>N</sub>2-f and non-cyclic TS for S<sub>N</sub>2-b. (R: Reactants, RC: Reactant Complex, PC: Product Complex, P: Products)