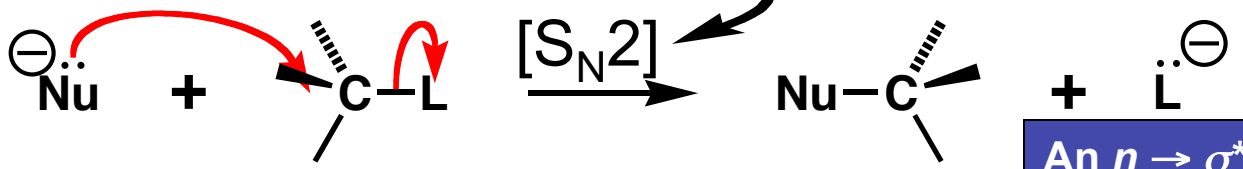
Two Mechanistic Pathways for Substitution

One step mechanism: [S_N2] = [A_N] + [D_N]

This symbol means bimolecular nucleophilic substitution

[S_N2] involves σ-bond making & breaking

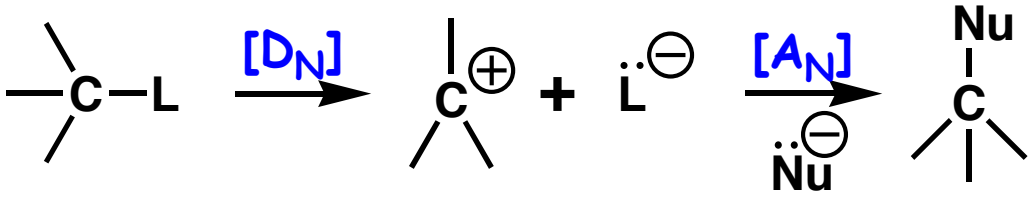


An *n* → σ* σ-type interaction

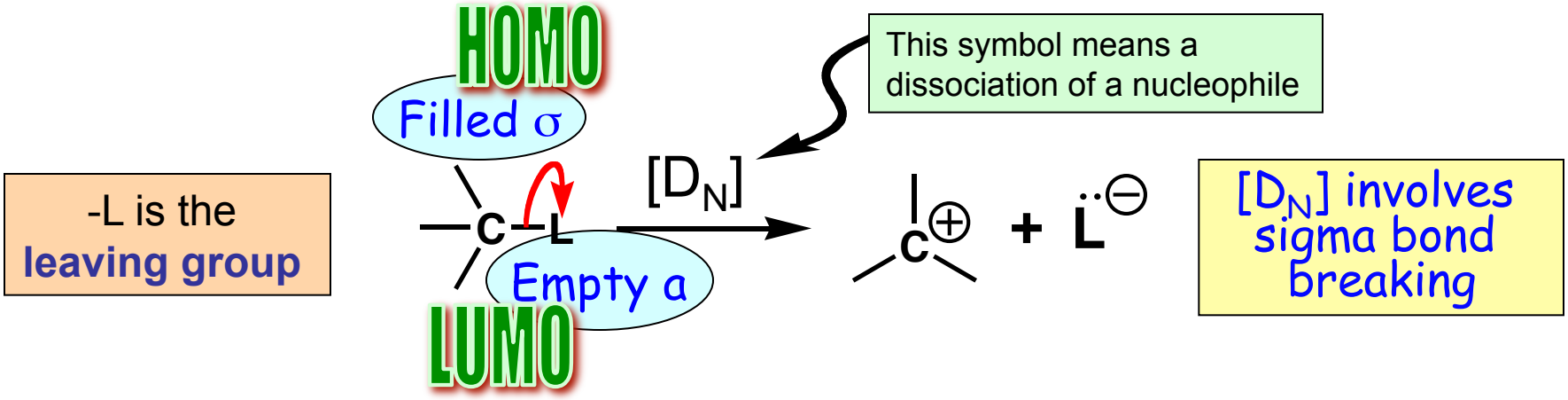
Here bond making and breaking take place at the same time - a **concerted** process. Any one-step process is its own elementary step. So we'll call the elementary step that results from **concerted** combination of [A_N] + [D_N] the [S_N2] step, which stands for **nucleophilic, bimolecular substitution**. It's bimolecular because two species must come together. We need to re-consider the frontier orbitals involved in this new elementary step. The tail of the first arrow implies the filled orbital (HOMO) is a non-bonded electron pair, *n*. The head of the first arrow points to the empty orbital (LUMO, σ*) that accepts the electron pair. The empty orbital may not be obvious until you realize that the C-L sigma bond breaks, as implied by the tail of the second arrow. Sigma bond breaking would result upon filling σ* with the electron pair from *n*. The frontier orbitals align coaxially (a σ-type interaction).

Two step mechanism: [S_N1] = [D_N] then [A_N]

The second pathway is a **sequential** combination of [D_N] followed by [A_N]. This **sequential, two-step** mechanistic pathway is called **unimolecular nucleophilic substitution**, or [S_N1]. The slowest step is the unimolecular [D_N]. process, hence the "unimolecular" in the name. The most important thing to realize is that the [S_N1] pathway will only be available if a stable carbocation can form.



Substitution Mechanisms Require New Elementary Steps: Nucleophile Dissociation [D_N] & the Nature of Leaving Groups



[D_N] involves a $\sigma \rightarrow a$ "no-bond" interaction

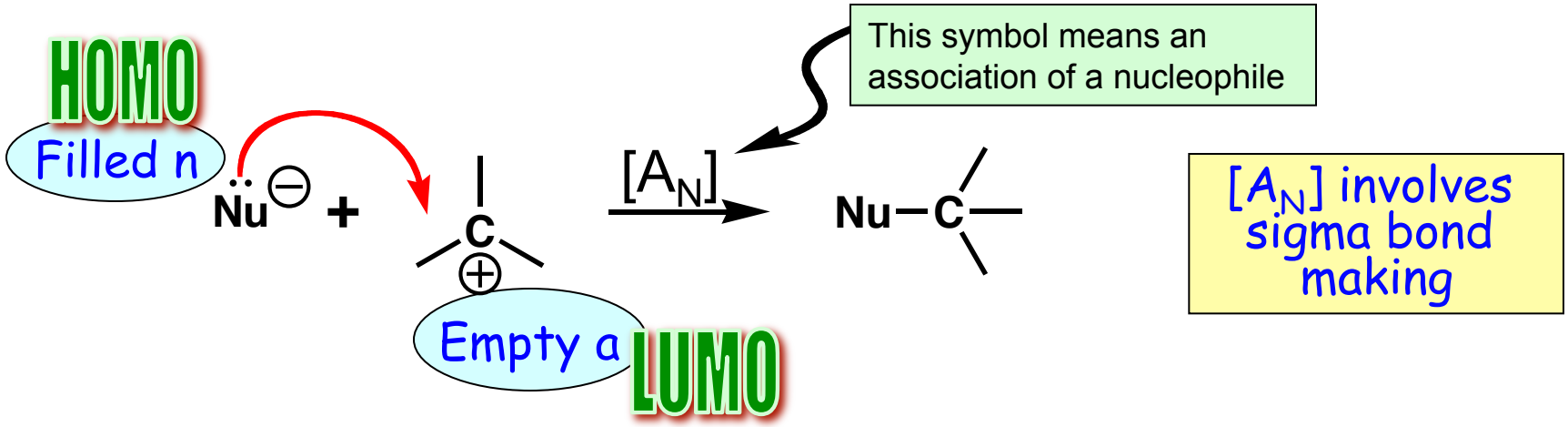
Curved Arrows Imply the Frontier Orbitals

Curved arrows indicate the HOMO-LUMO pair (Frontier Orbitals) involved in an elementary step. The tail of the arrow implies the filled orbital (HOMO) is σ electron pair. The head of the arrow points to an atom on the leaving group (L) suggesting that an atom-centered empty orbital (LUMO, *a*) accepts the electron pair. The process produces no new bonding interactions. **A good leaving group will have a high energy σ and low lying *a*.**

empty / filled	σ*	a	π*
σ	σ→σ*	σ→a	σ→π*
n	n→σ*	n→a	n→π*
π	π→σ*	π→a	π→π*

Substitution Mechanisms Require New Elementary Steps: Nucleophile Association [A_N]

$\ddot{Nu}^{\ominus}$ is the nucleophile



[A_N] involves an n → *a* *σ-type* interaction

Curved Arrows Imply the Frontier Orbitals

Curved arrows indicate the HOMO-LUMO pair (Frontier Orbitals) involved in an elementary step. The tail of the arrow implies the filled orbital (HOMO) is non-bonded electron pair, *n*. The head of the arrow points to an empty orbital on the carbocation, suggesting that an atom-centered empty orbital (LUMO, *a*) accepts the electron pair. **A good nucleophile will have a high energy *n*.**

empty / filled	σ*	a	π*
σ	σ→σ*	σ→a	σ→π*
n	n→σ*	n→a	n→π*
π	π→σ*	π→a	π→π*