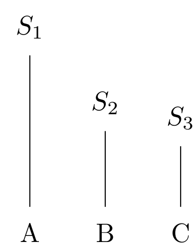

Figure 1: Multi-pathway fragmentation signals in the mass spectrometer.

Single and multi-pathway fragmentations

Scope

We want a relation between multi-path fragmentation probabilities and single-path fragmentation probabilities.

Notation

- A is the intact cluster, B and C are fragments for two different pathways
- P_B = probability of fragmentation $A \to B$ in single-pathway
- P_C = probability of fragmentation $A \to C$ in single-pathway
- P_1 = probability of survival for A
- P_2 = probability of fragmentation $A \to B$ in multi-pathway
- P_3 = probability of fragmentation $A \to C$ in multi-pathway

Discussion

Imagine that we perform simultaneously two different single-pathway evolutions, one for $A \to B$ channel and the other for $A \to C$ channel. We have four different possible outcomes:

1. Cluster A survives in both evolutions, with probability $(1 - P_B)(1 - P_C)$
2. Cluster A fragments in the first evolution but not in the second one, with probability $P_B(1 - P_C)$
3. Cluster A fragments in the second evolution but not in the first one, with probability $P_C(1 - P_B)$
4. Cluster A fragments in both evolutions, with probability $P_B P_C$

Now, let us find the correspondence of these four situations with the three possible scenarios in multi-path evolution:

1. Cluster A survives: it coincides with previous outcome 1
2. Cluster A fragments into B: it corresponds to outcome 2, plus outcome 4 when fragmentation $A \to B$ happens before $A \to C$
3. Cluster A fragments into C: it corresponds to outcome 3, plus outcome 4 when fragmentation $A \to C$ happens before $A \to B$

Now, before writing explicitly P_1, P_2 and P_3, we are just missing an expression for the probability that in outcome 4 one fragmentation happens before the other one. In order to do that it is reasonable to set this probability proportional to the fragmentation probability in single-pathway evolution:

- Probability that $A \to B$ happens before $A \to C$ is proportional to P_B
- Probability that $A \to C$ happens before $A \to B$ is proportional to P_C

Since the sum of these two situations must sum up to 1, it is easy to calculate the proportionality factor N:

$$NP_B + NP_C = 1 \quad \Rightarrow \quad N = \frac{1}{P_B + P_C} \,. \tag{1}$$

Finally, we have:

$$P_1 = (1 - P_B)(1 - P_C) \tag{2}$$

$$P_2 = P_B(1 - P_C) + \frac{P_B}{P_B + P_C} P_B P_C \tag{3}$$

$$P_3 = P_C(1 - P_B) + \frac{P_C}{P_B + P_C} P_B P_C \tag{4}$$

The sum $P_1 + P_2 + P_3 = 1$, as expected. The instrument signals S_i (Figure 1) are proportional to these probabilities, with proportionality factor $\alpha = S_1 + S_2 + S_3$: $S_i = \alpha P_i$.