Figure 5: Simulated region of APi-TOF mass spectrometer. The dashed lines identify the zones with different voltage configurations. The thin solid line emulates a single realization trajectory of cluster. The zone lengths are not to scale.

The vibrational density of states is then computed using the harmonic approximation, which is most likely the biggest source of errors in the evaluation of the cluster survival probability. (See next section for a sensitivity analysis on the effect of the varying the vibrational frequencies).

3 Results

The simulation region involves only a portion of the total length of the APi-TOF mass spectrometer. Specifically, the simulations take place in the most critical region, between the end of the first chamber and the second one, where the pressure values make fragmentation possible. Before this region the collisions are not energetic enough, while after the carrier gas is so sparse that no collision happens [16].

In Fig. 5 we have a sketch of the simulated region. We subdivide the simulation region into 5 sections with different electric field and pressure values. Region I is at the end of the first chamber, region II defines the interface between the first and the second chambers and regions III, IV and V are located in the second chamber of the APi. The pressure in the first region is \( P_1 \), while in the regions III, IV and V it is \( P_2 \). In the region II, where the skimmer is located, the pressure is treated as a gradient, changing continuously from \( P_1 \) to \( P_2 \). The electric field takes different values in the regions I, III, IV and V, while in II it is set to zero.

The voltage and pressure configuration, that defines the electric fields and the pressures inside the APi chambers, used in the CLOUD10 experiments, are the following:

- \( P_1 = 201 \) Pa
- \( P_2 = 2.96 \) Pa
- \( E_1 = 7189 \) V/m
- \( E_2 = 8049 \) V/m
- \( E_3 = 1804 \) V/m
- \( E_4 = 1104 \) V/m

We will use this voltage configuration and these pressures in our simulations. It is important to notice here that the electric field takes very different values in different sections, up to 3 orders of magnitude, which will affect the fragmentation positions as we will see (Fig. 12). We assume low amplitude of the oscillating electric field in the quadrupole of region IV. In this regime, the transverse motion of the cluster is negligible and does not affect the fragmentation probability. In this study the cluster fragmentation energy \( E_f \) is treated as a free parameter. This allows us to explore the behaviour of cluster survival probability as a function of \( E_f \) on a large energy range. Moreover, keeping \( E_f \) as a variable is also useful since its computation by quantum chemistry calculations (especially low-level methods such as PM7 used here) is affected by large errors.

The clusters studied here are formed by one bisulfate anion, one sulfuric acid molecule and at least one HOM molecule. The clusters are assumed to fragment by losing one HOM, as follows:

\[
(HSO_4^-)(H_2SO_4)_n(HOM_{10})_m! \\
(HSO_4^-)(H_2SO_4)_n(HOM_{10})_{m-1}+(HOM_{10})
\]

with \( n = 1, 2, m = 1, 2, 3 \) and HOM\(_{10}\) is the structure shown in Fig. 1. Our specific choice for HOM is not unique: this is one among many potential HOM produced in the \( \text{pinene} + \text{O}_3 \) reaction. The compound chosen is broadly representative of autoxidation products as it contains both hydroperoxide, ketone and carboxylic acid groups. The clusters have been constructed by first maximizing H-bonds between the \( H_2SO_4^- \)