2 Method

The model computes the probability of fragmentation of a single negatively-charged cluster from a large number ($\approx 10^3$) of independent stochastic realizations of its dynamics in the API.

The algorithm of the code is described by the simplified flowchart shown in Fig. 3. We give here a brief description. For detailed description see Zapadinsky et al [16].

The dynamics starts with the ionized cluster accelerating in the mass spectrometer under the effect of an electric field generated by the electrodes inside the API. While moving, a random time interval to the next collision is computed from the cumulative distribution function $P_{\text{coll}}(t)$, which expresses the probability to encounter a collision after a time $t$:

$$P_{\text{coll}}(t) = 1 - e^{-\frac{t}{\tau_{\text{c}}}} \int_0^\infty \mathcal{F}(v)(t^2) \, dt^3. \tag{1}$$

Here, $\tau_{\text{c}}$ is the collision frequency which depends on the cluster velocity $v$, $w$ if $t < 0$ is the moment when the previous collision occurred. Simultaneously, another random time interval is computed for the fragmentation event from a Poisson distribution, which corresponds to the time-dependent survival probability $P_{\text{surv}}$ after collision:

$$P_{\text{surv}}(t) = 1 - P_{\text{frag}} = e^{-k(\Delta E)t}, \tag{2}$$

where $P_{\text{frag}}$ is the fragmentation probability and $k$, the fragmentation rate constant, is the inverse of the statistical average of fragmentation time, which depends on the cluster excess energy $\Delta E$ beyond its fragmentation energy threshold. The fragmentation time is interpreted as the time the cluster spends intact before fragmenting. The fragmentation rate constant is derived from equilibrium condition between fragmentation and recombination processes using the detailed balance condition [16].

At this point, if the time required by the cluster to escape from the simulated region of the mass spectrometer is less than both the collision...