Supplement

QqQ-MS number of collisions

By changing the CID gas pressure the number of collisions (#coll) in the CC can be varied, which is expected to influence fragmentation patterns. Figure A1 shows the dependence of the abundance of protonated α-pinene ($C_{10}H_{17}^{+}$, m/z=137) on the CID gas pressure, at U_{CC} = 50 V.

In classical collision theory, the mean free path λ of a molecular beam through a collision gas is correlated to a relative loss of beam intensity (A1).

$$-\frac{dI}{Idx} = \frac{1}{\lambda} \qquad \text{(A1)}$$

Integrated over the full length x of the CC, this equation leads to equation (A2).

$$I = I_0 e^{-\frac{l}{\lambda}} = I_0 e^{-\#coll} \qquad \text{(A2)}$$

Since typical bond energies are much smaller than the maximum collision energy at U_{CC} = 50 V, it is assumed that every collision leads to a loss of a parent ion. Therefore, the exponent $\frac{l}{\lambda}$ is the best estimate as well as the lower limit for #coll and can easily be measured by changing the CID gas pressure at a constant U_{CC}. Comparison of the measured lower limits with calculations based on a Langevin collision theory shows that above $U_{CC} \approx 3$ V the number of collisions stays constant according to a hard sphere collision model. Therefore, by changing from $0.4 \cdot 10^{-3}$ hPa to $2.7 \cdot 10^{-3}$ hPa CID gas pressure, CID-conditions can be changed from a single collision event to a multiple collision fragmentation process with a maximum of about 7 collisions.

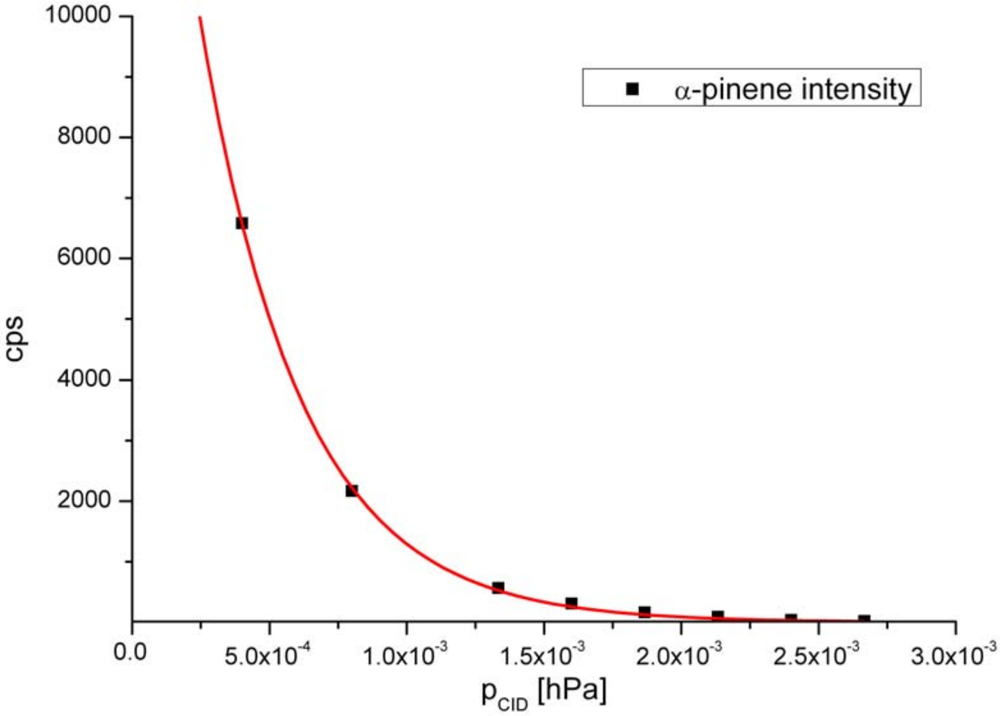

Figure S1. Signal dependence as a function of the CID argon pressure. Data obtained for α-pinene at U_{CC} = 50 V. The red line shows the best exponential fit.