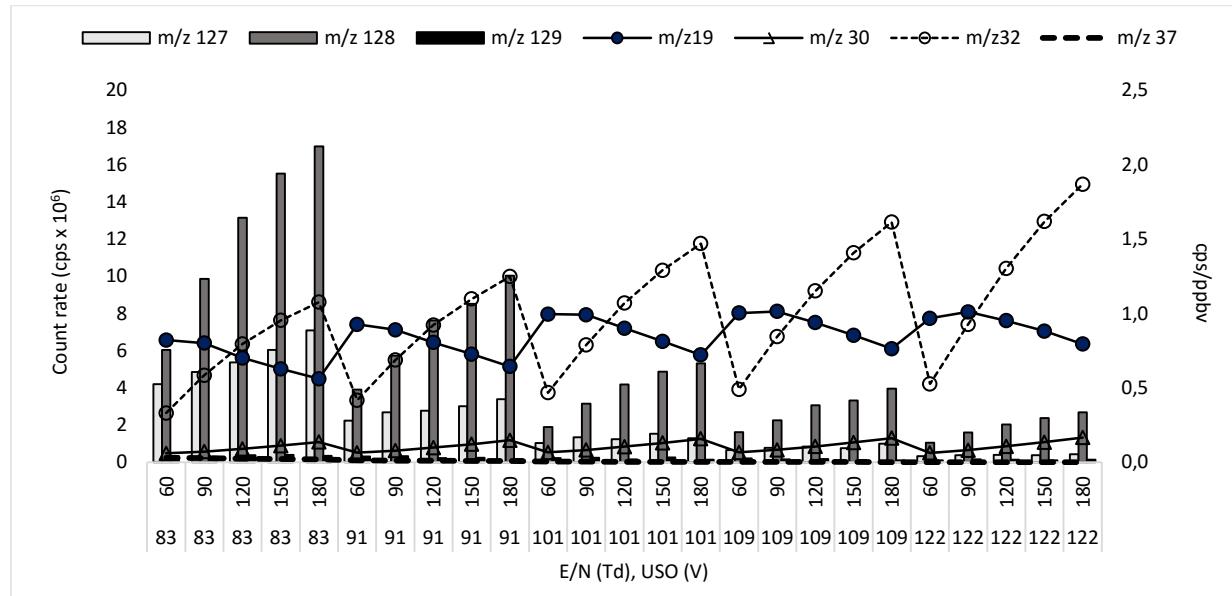
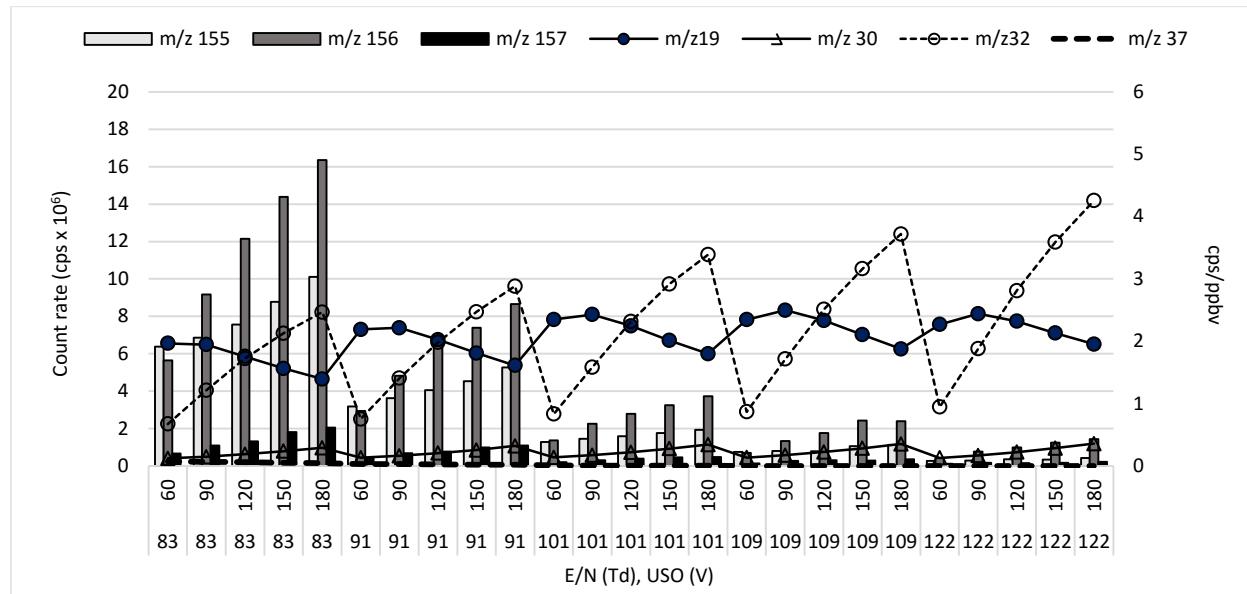
The next graphs in figure S1 show the variability at low water flow (2 sccm) of the key source ions comprising H_3O^+ (m/z 19), O_2^+ (m/z 32), NO^+ (m/z 30) and $H_2O.(H_3O)^+$ (m/z 37) as a function of E/N. Due to excessive water clusters at low E/N found at 6 sccm (HWF), the primary ion (H_3O^+) was saturated. The intensity of $H_2O.(H_3O)^+$ decreased, when E/N increased because a de-clustering effect occur at higher electric field (Blake et al. 2009). Higher intensities were observed at low water flow for all n-alkanes. Sensitivities increased when O_2^+ increased.

a

b

c

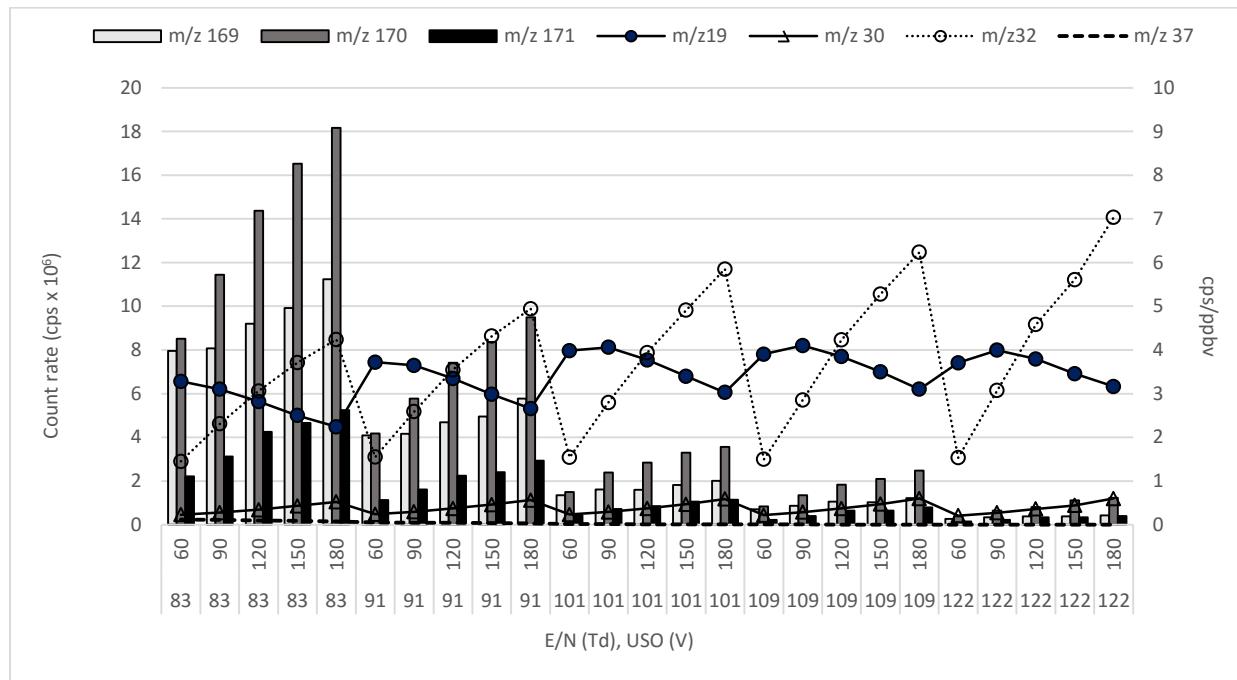



Figure S1. Intensity of signals (counts per second, cps) for H_3O^+ (m/z 19), NO^+ (m/z 30), O_2^+ (m/z 32), $H_2O.(H_3O)^+$ (m/z 37) and sensitivities (cps/ppbv) for *n*-alkanes at low water flow (2 sccm). **a.** *n*-nonane, **b.** *n*-undecane and **c.** *n*-dodecane. Data are shown for tests at five E/N ratios (83, 91, 101, 109 and 122 Td) and five U_{SO} voltages (60, 90, 120, 150 and 180).

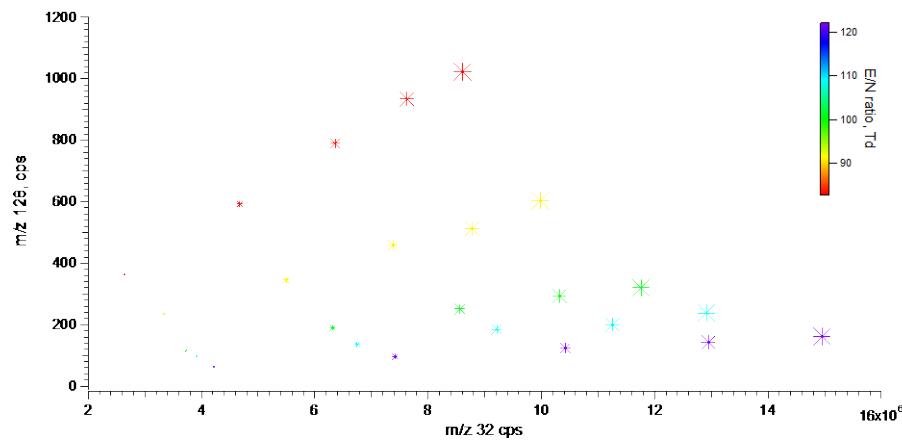
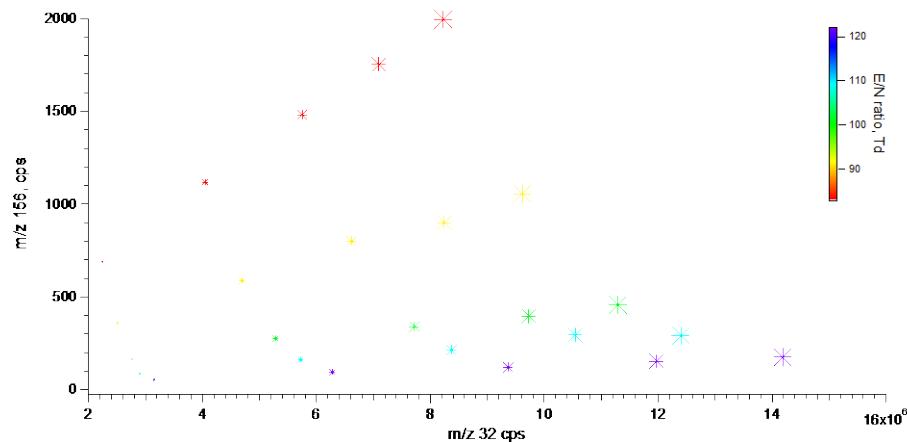
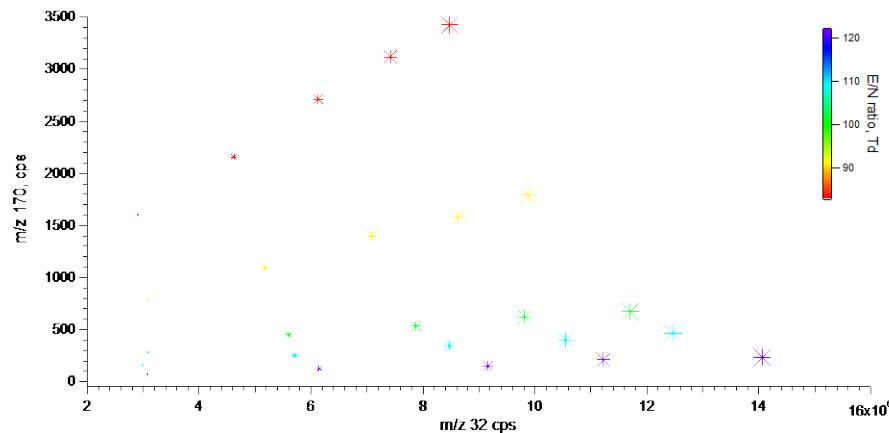



Figure S2. Intensities of m/z 32 (O_2^+) vs. intensities of charge transfer products for (a) *n*-nonane (m/z 128), (b) *n*-undecane (m/z 156) and (c) *n*-dodecane (mz/ 170). Marker size illustrates the U_{SO}: Smallest 60 V and largest 180 V.

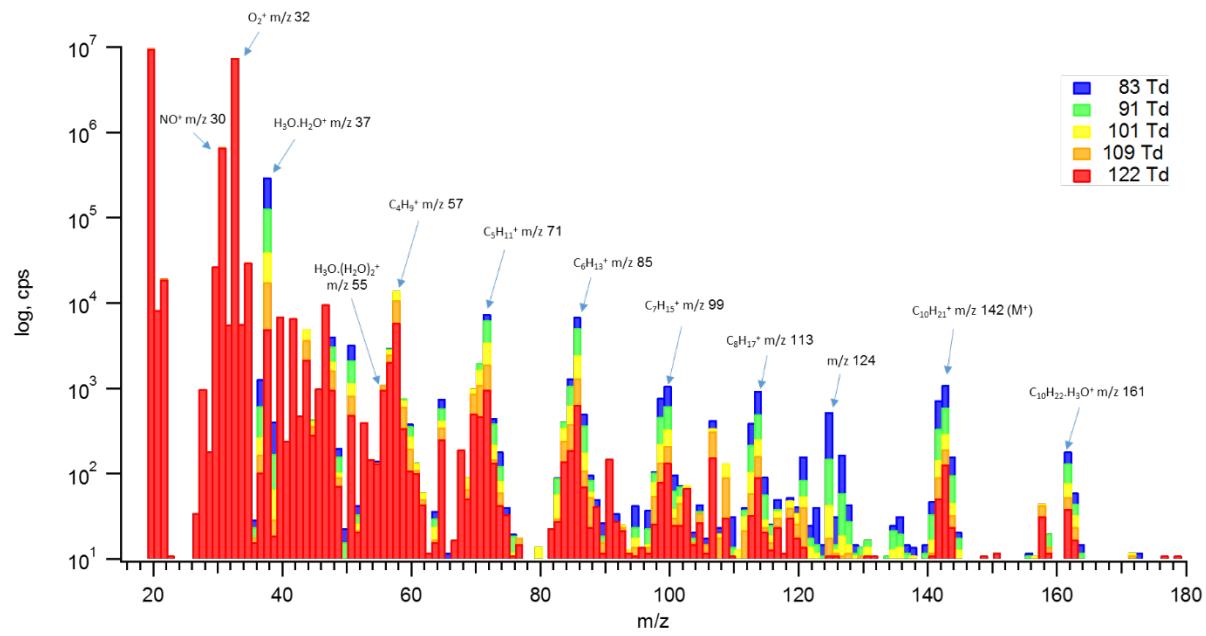



Figure S3. Mass spectra of *n*-decane. WF2, USO 60 V. E/N ratios from 83 to 122 Td.

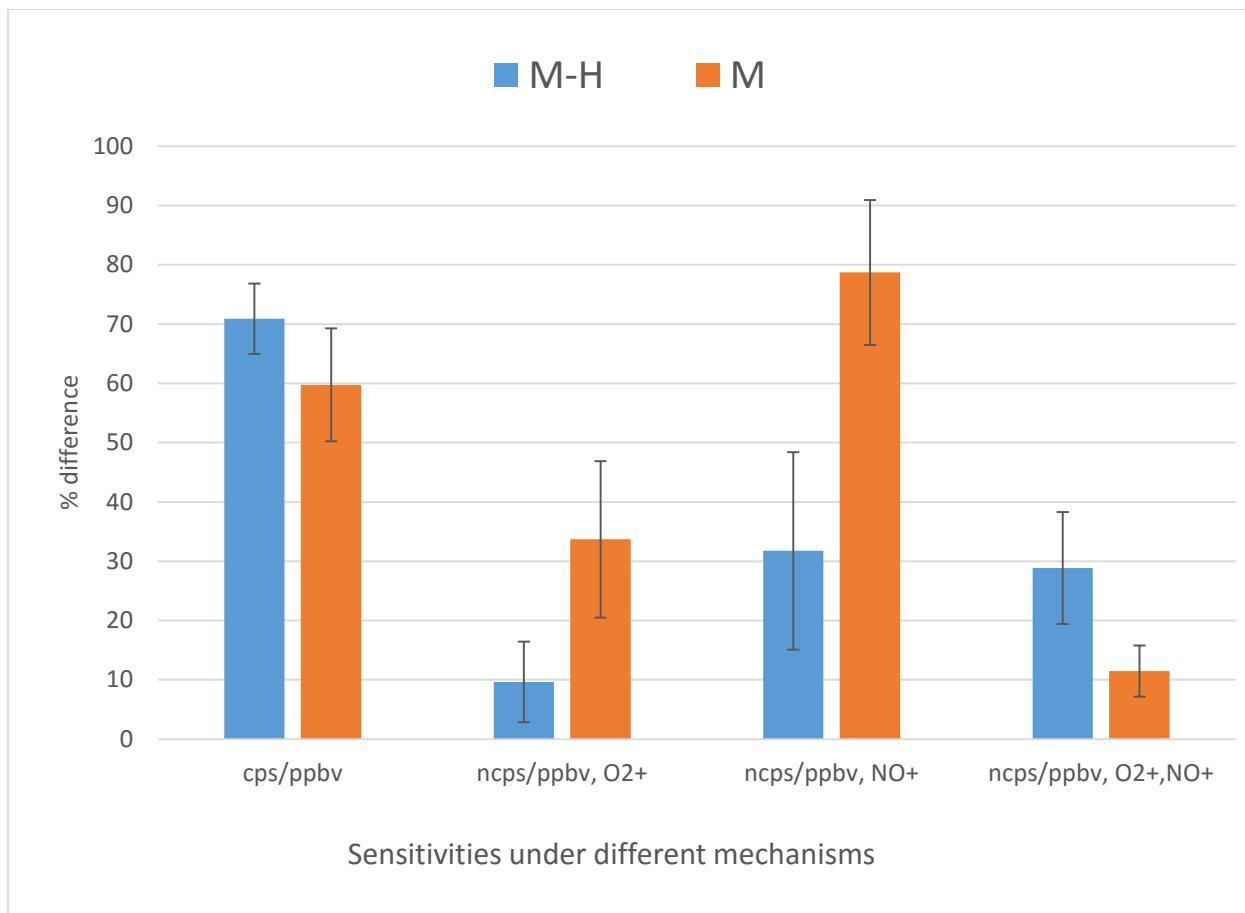



Figure S4. Difference of absolute sensitivities (cps/ppbv) and normalized sensitivities (ncps/ppbv) between two sets of experiments in percentage. Average and standard deviation (bars) including data for *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane. The dominant mechanism for these *n*-alkanes was CT.

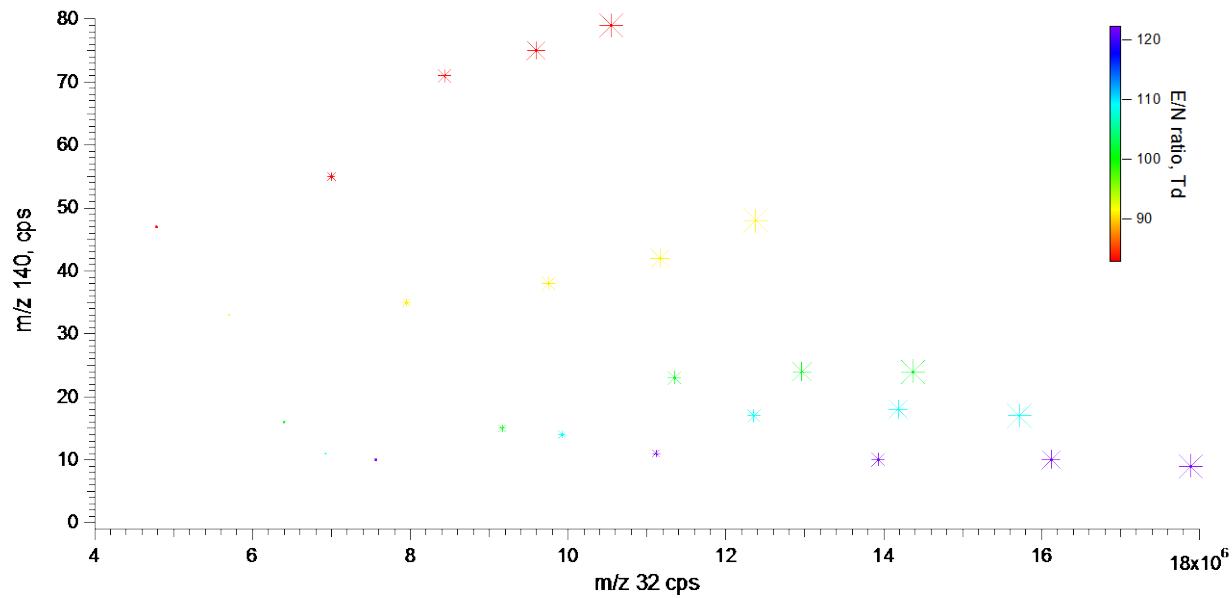
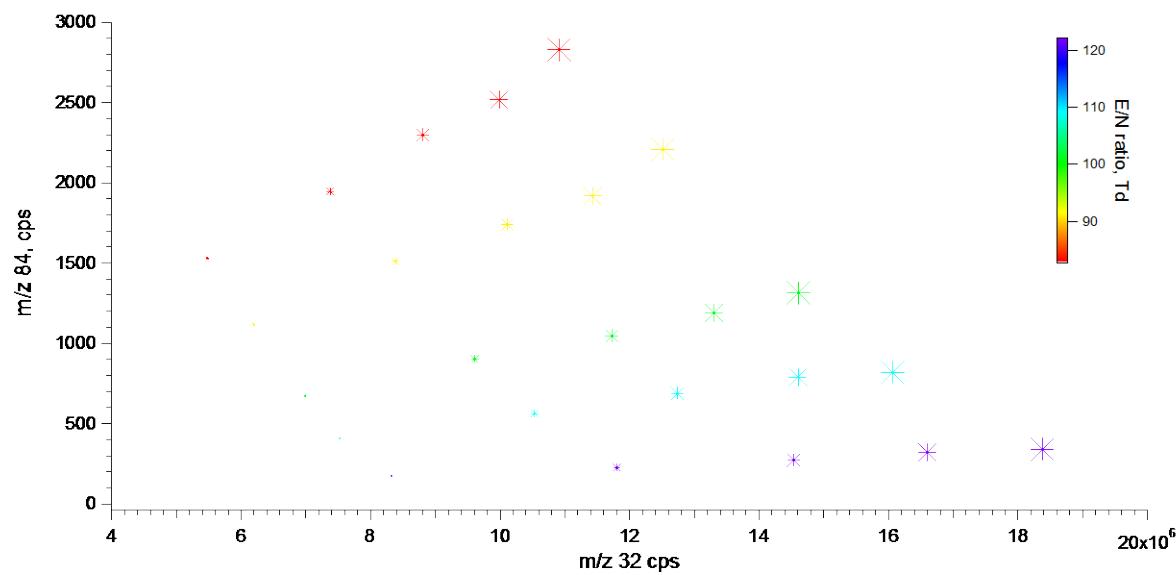



Figure S5. Intensities of double hydride abstraction for (a) *n*-decane (m/z 140) and (b) *n*-hexane (m/z 84) vs. O_2^+ (m/z 32). Marker size illustrates the U_{SO}: Smallest 60 V and largest 180 V.