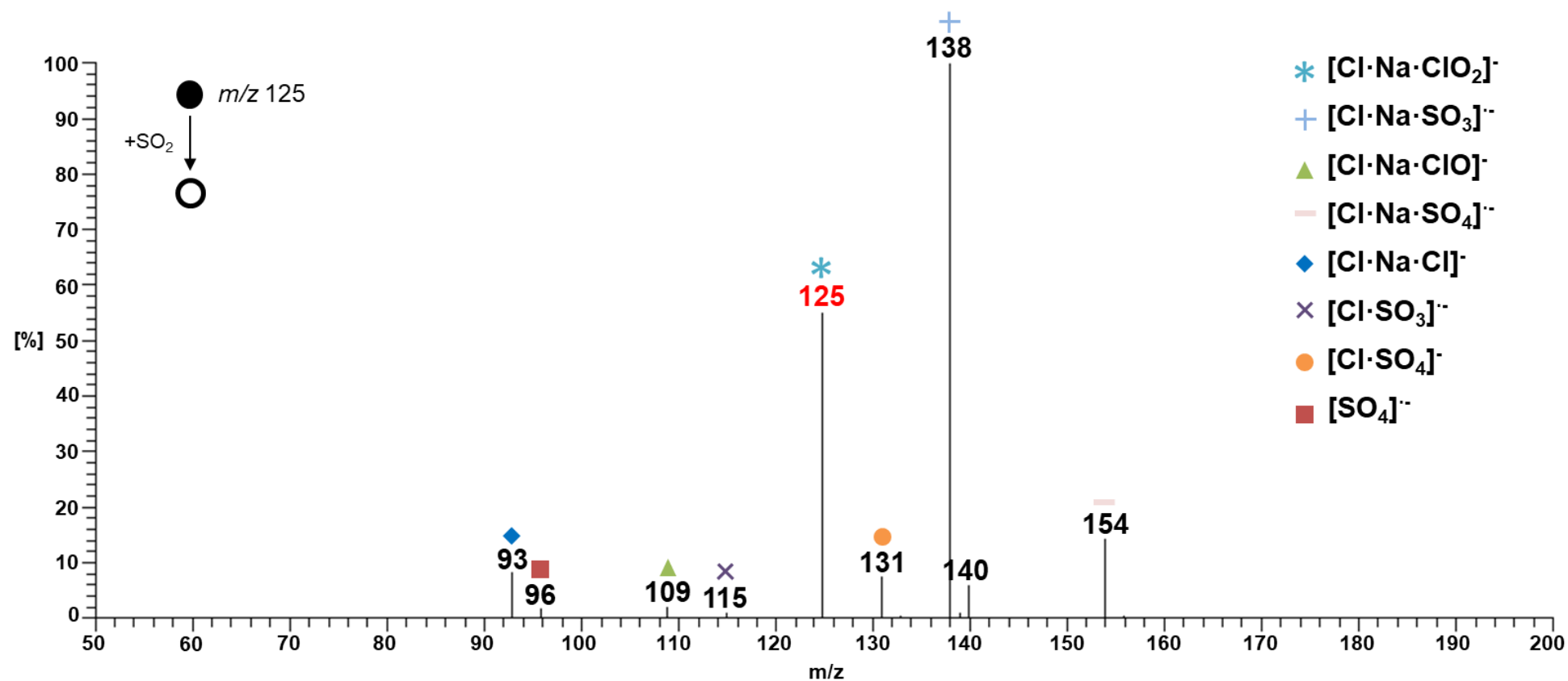
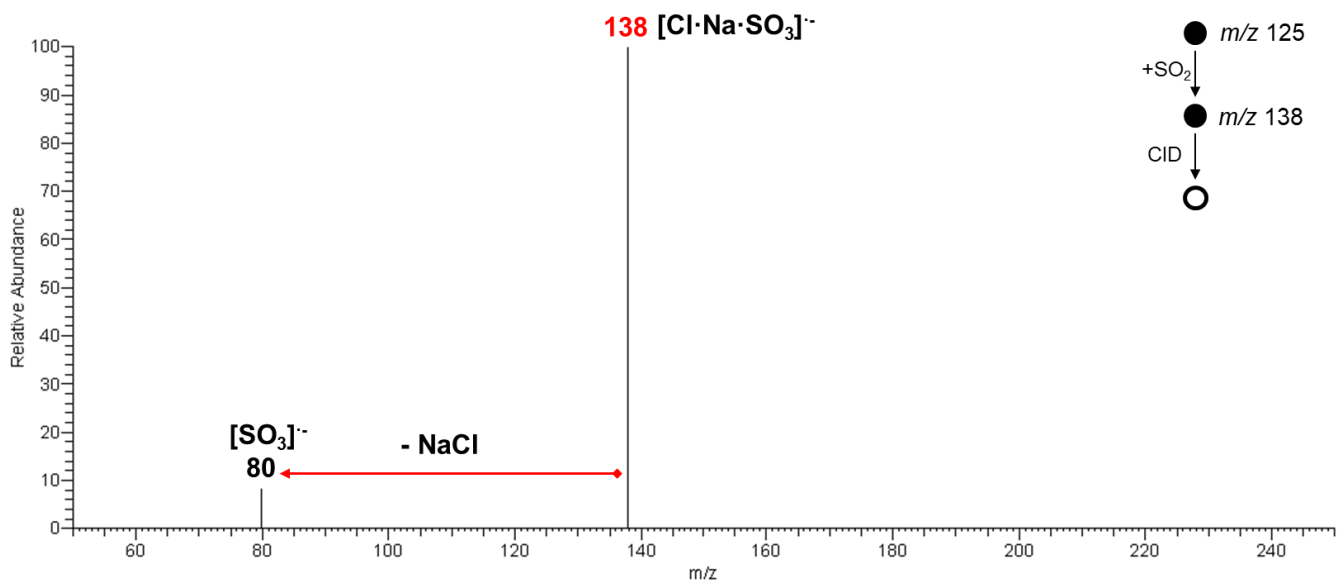


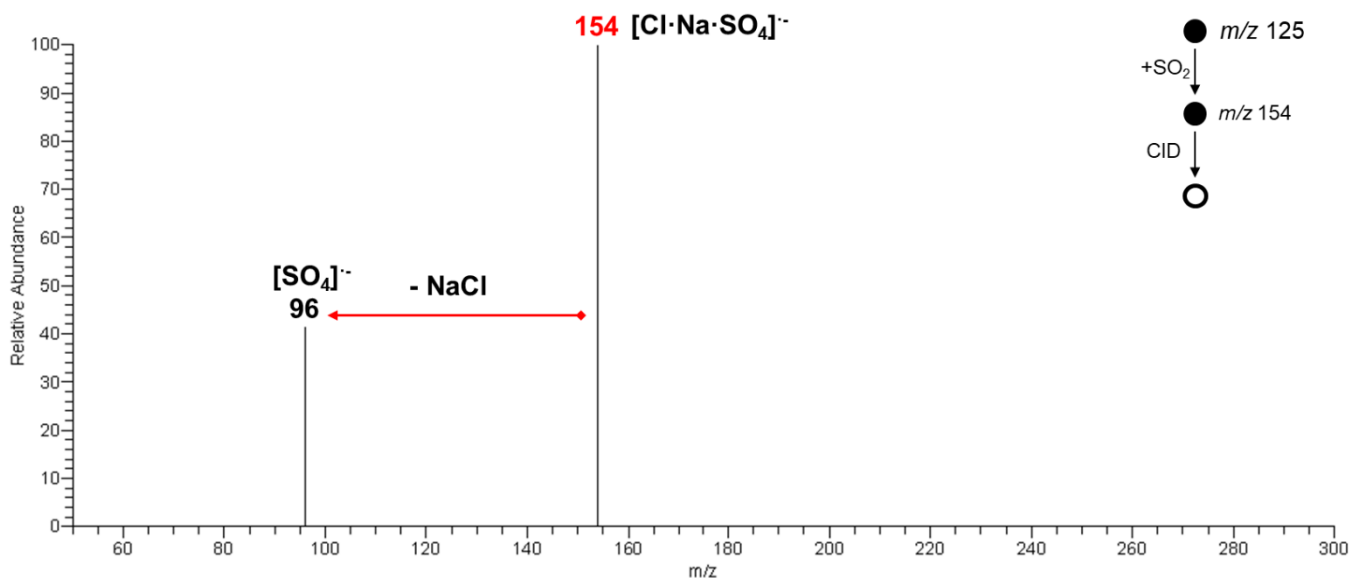
**Figure S1.** IT full-scan mass spectrum of a millimolar solution containing  $NaClO_2$  salt in  $H_2O/CH_3CN$  (V/V% 1:1) acquired in the a) 20-100 and b) 100-500  $m/z$  range. In spectrum a) ions at  $m/z = 46$  and  $62$  are attributed to  $NO_2^-$  and  $NO_3^-$  respectively.



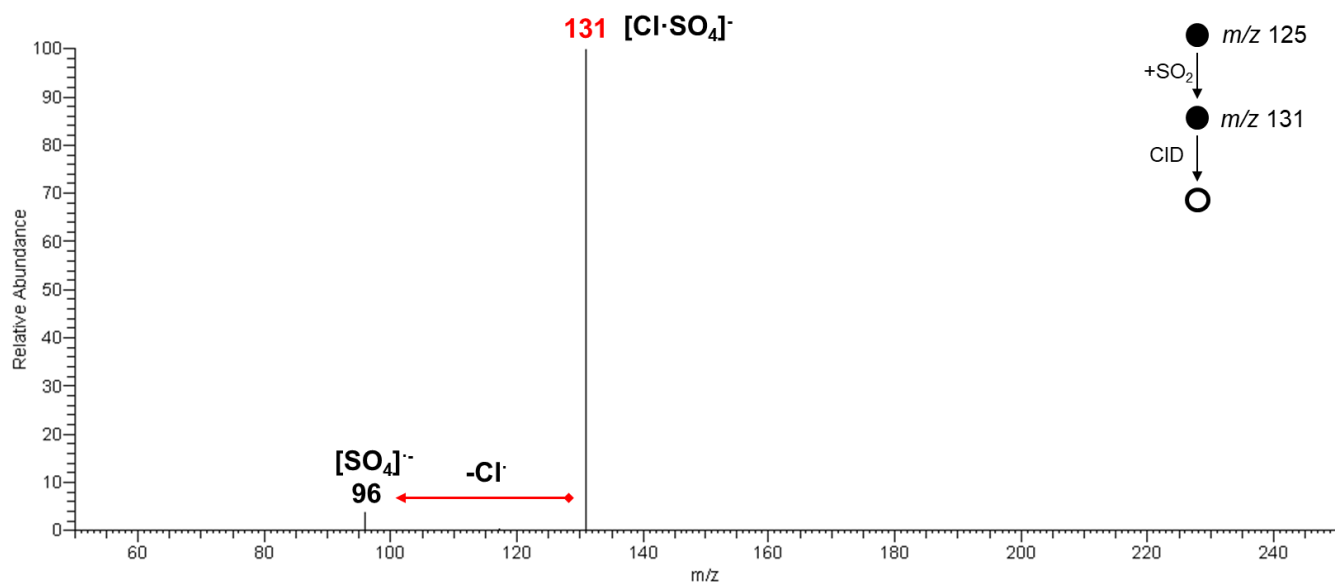
**Figure S2.** IT mass spectrum of the ion-molecule reaction between isolated  $[Cl·Na·ClO_2]^-$  cluster ion at  $m/z$  125 (in red) and  $SO_2$  at an activation time (AT) of 700 ms and a  $P_{SO_2} = 1.97 \times 10^{-7}$  Torr.



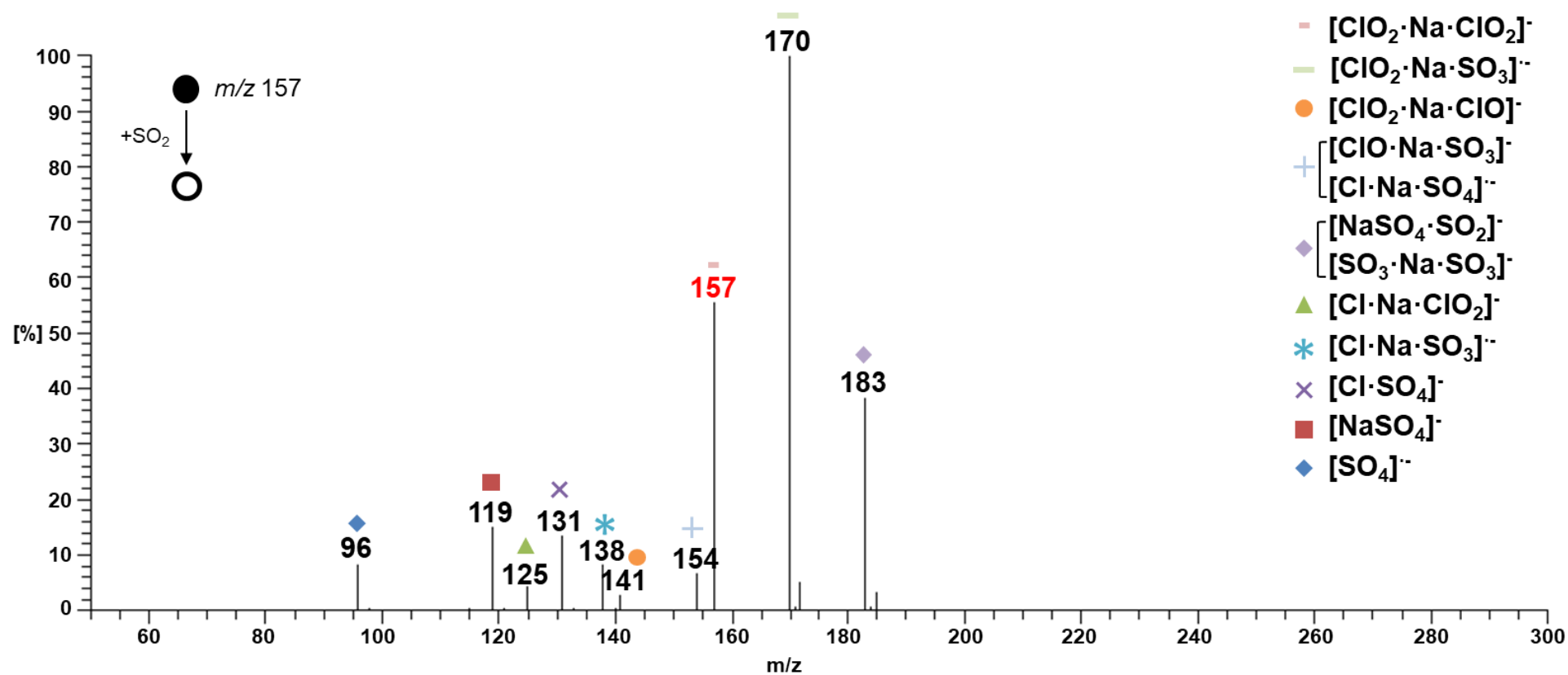
**Figure S3.** IT-CID mass spectrum of  $[\text{Cl}\cdot\text{Na}\cdot\text{SO}_3]^-$  product ion at  $m/z$  138 (in red)  $\text{MS}^n$  -isolated from the reaction of  $[\text{Cl}\cdot\text{Na}\cdot\text{ClO}_2]^-$  reactant ion ( $m/z$  125) with  $\text{SO}_2$ .



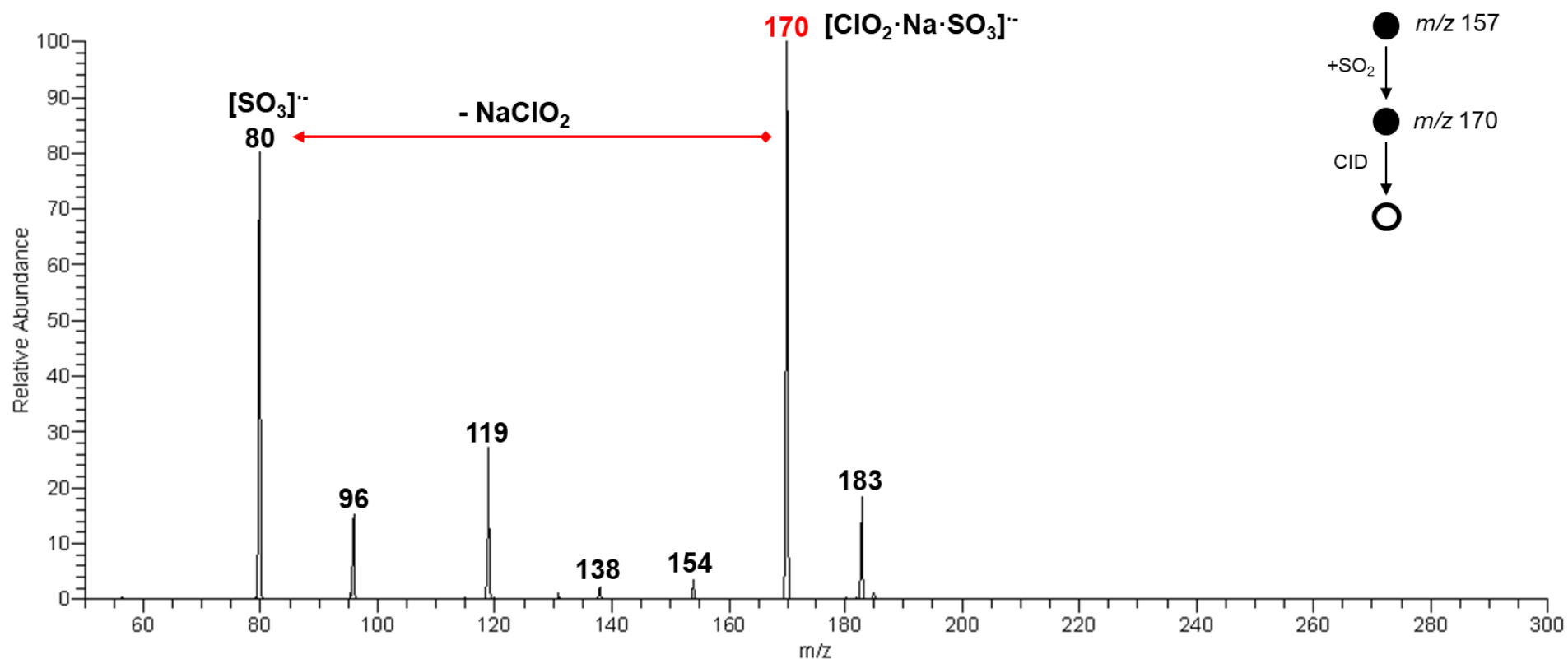
**Figure S4.** IT-CID mass spectrum of  $[\text{Cl}\cdot\text{Na}\cdot\text{SO}_4]^-$  product ion at  $m/z$  154 (in red)  $\text{MS}^n$  -isolated from the reaction of  $[\text{Cl}\cdot\text{Na}\cdot\text{ClO}_2]^-$  reactant ion ( $m/z$  125) with  $\text{SO}_2$ .



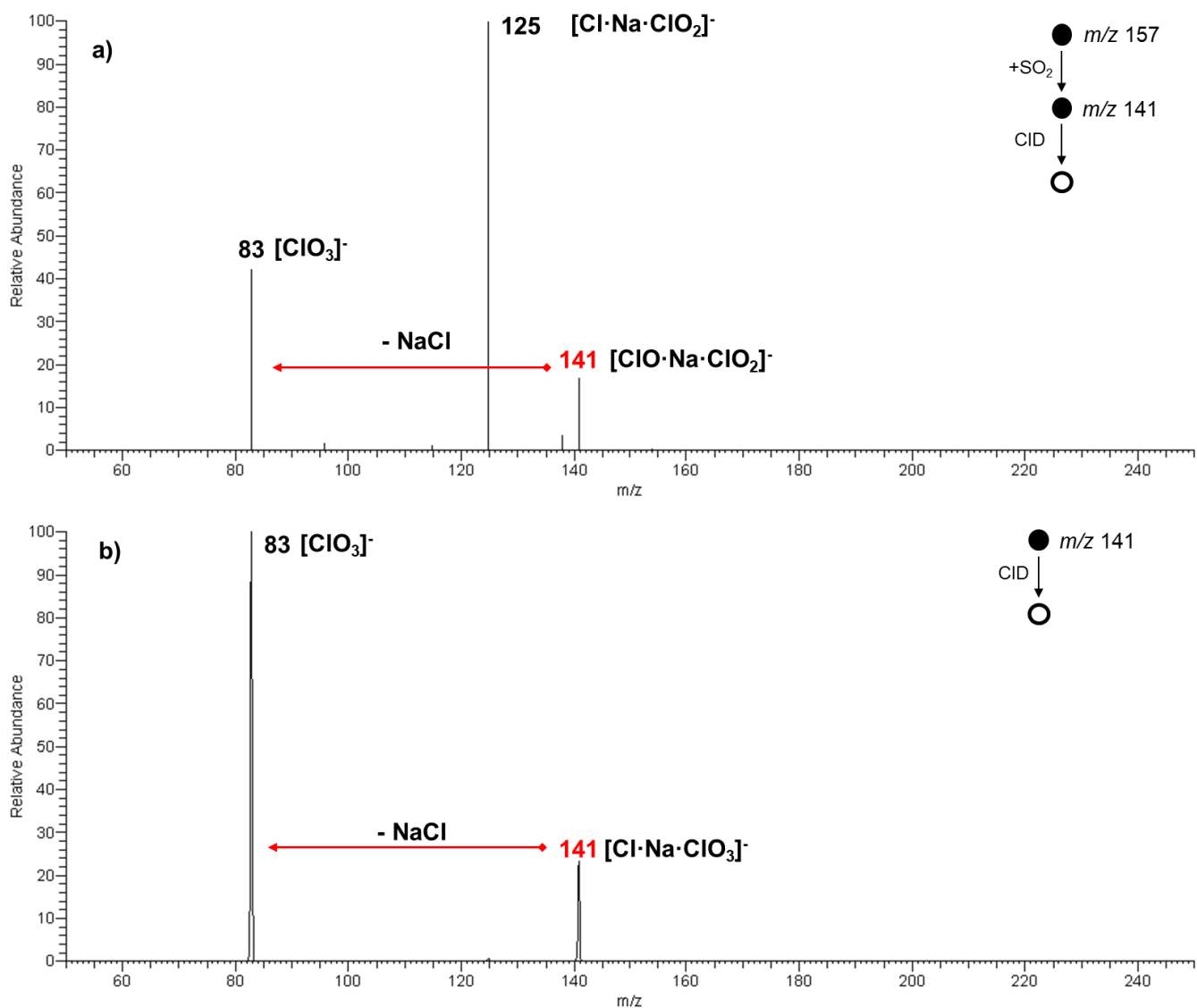
**Figure S5.** IT-CID mass spectrum of  $[\text{Cl}\cdot\text{SO}_4]^-$  product ion at  $m/z$  131 (in red)  $\text{MS}^n$ -isolated from the reaction of  $[\text{Cl}\cdot\text{Na}\cdot\text{ClO}_2]^-$  reactant ion ( $m/z$  125) with  $\text{SO}_2$ .



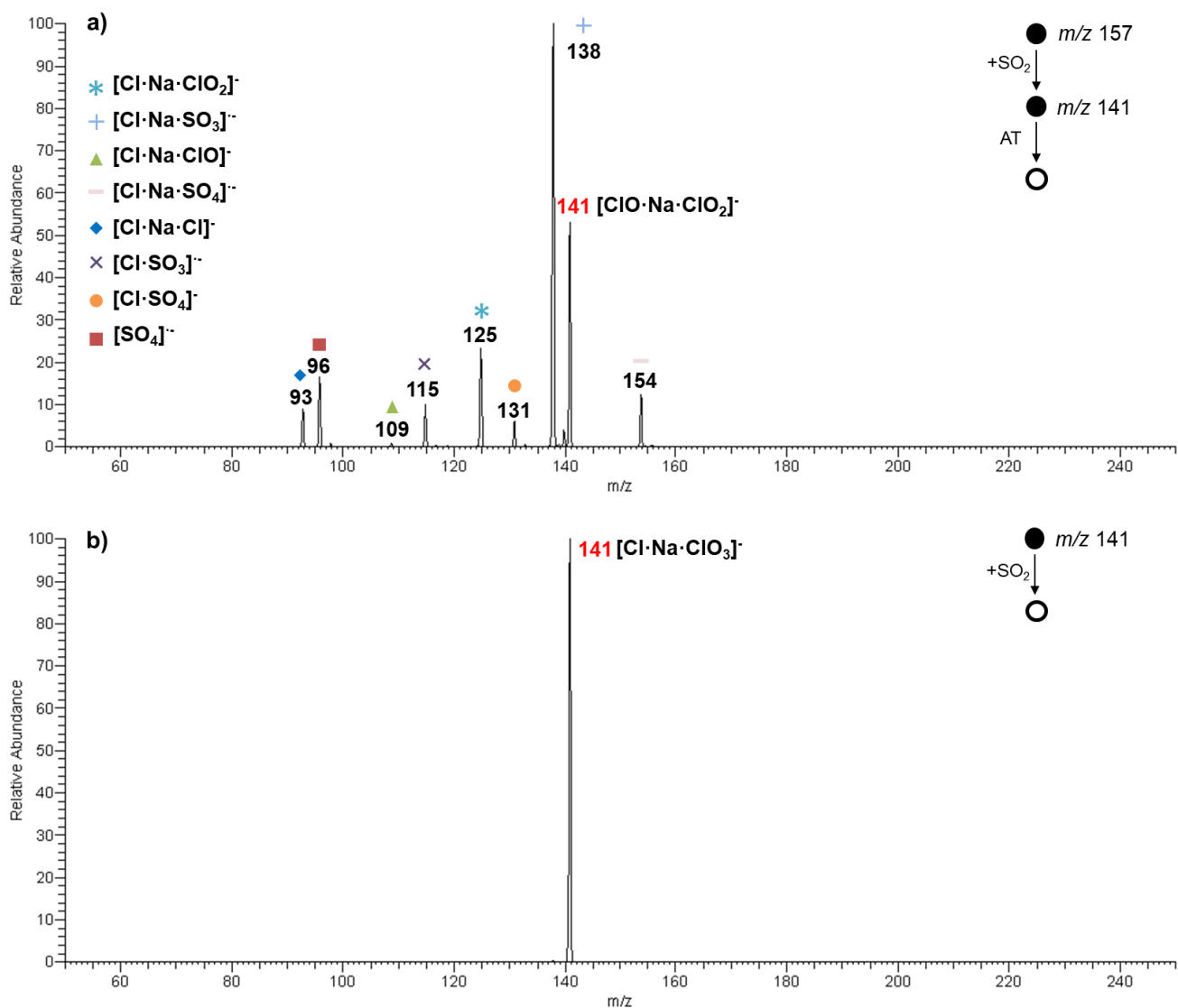
**Figure S6.** IT mass spectrum of the ion-molecule reaction between isolated  $[\text{ClO}_2 \cdot \text{Na} \cdot \text{ClO}_2]^-$  cluster ion at  $m/z$  157 (in red) and  $\text{SO}_2$  at an activation time (AT) of 350 ms and a  $P_{\text{SO}_2} = 1.64 \times 10^{-7}$  Torr.



**Figure S7.** IT-CID mass spectrum of  $[\text{ClO}_2 \cdot \text{Na} \cdot \text{SO}_3]^-$  product ion at  $m/z$  170 (in red)  $\text{MS}^n$ -isolated from the reaction of  $[\text{ClO}_2 \cdot \text{Na} \cdot \text{ClO}_2]^-$  reactant ion ( $m/z$  157) with  $\text{SO}_2$ . Minor ions at  $m/z$  96, 119, 138, 154, and 183 are consistent with the consecutive products of the reaction between  $[\text{ClO}_2 \cdot \text{Na} \cdot \text{SO}_3]^-$  ion at  $m/z$  170 and  $\text{SO}_2$ .

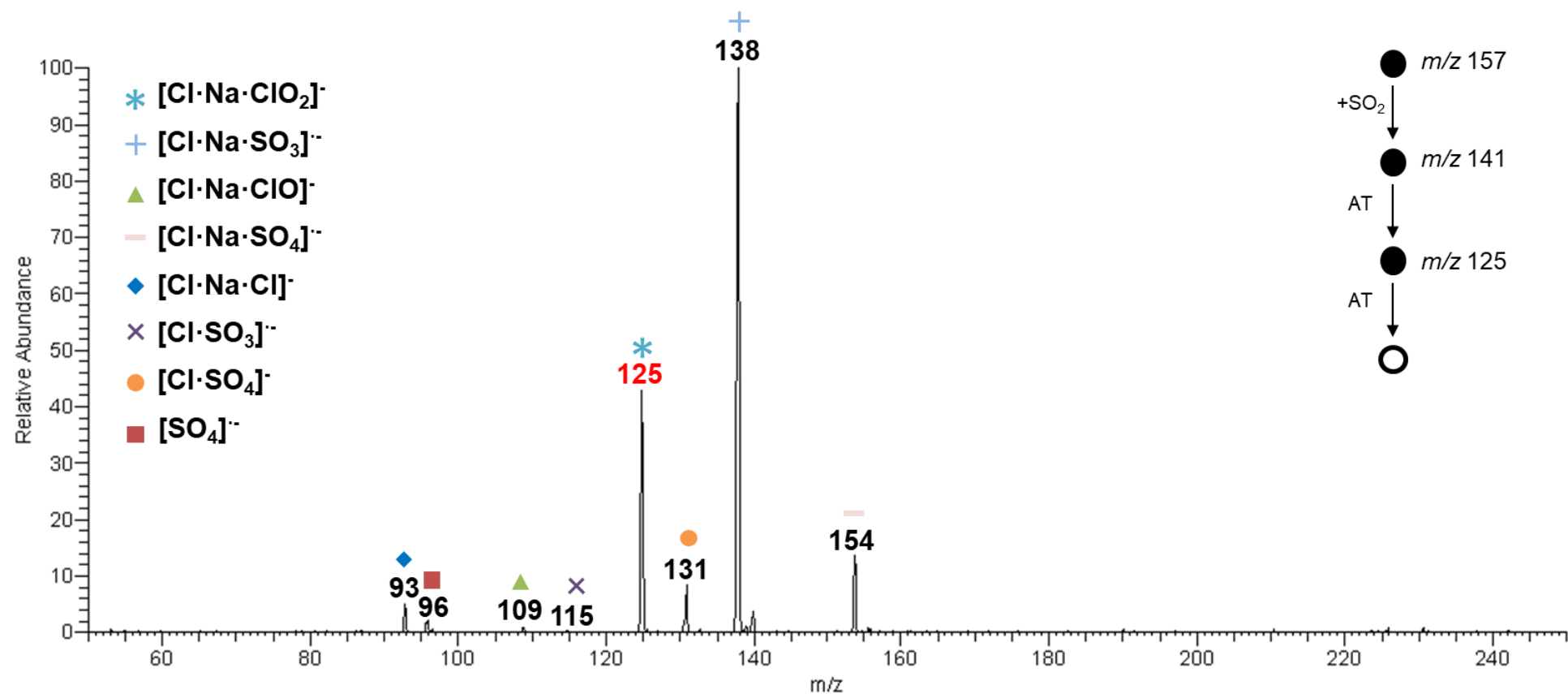


**Figure S8.** IT-CID mass spectrum of a)  $[\text{ClO} \cdot \text{Na} \cdot \text{ClO}_2]^-$  product ion at  $m/z$  141 (in red)  $\text{MS}^n$ -isolated from the reaction of  $[\text{ClO}_2 \cdot \text{Na} \cdot \text{ClO}_2]^-$  reactant ion ( $m/z$  157) with  $\text{SO}_2$  and b)  $[\text{Cl} \cdot \text{Na} \cdot \text{ClO}_3]^-$  standard ion at  $m/z$  141 (in red) obtained from a 1:1  $\text{NaCl}/\text{NaClO}_3$  millimolar solution.

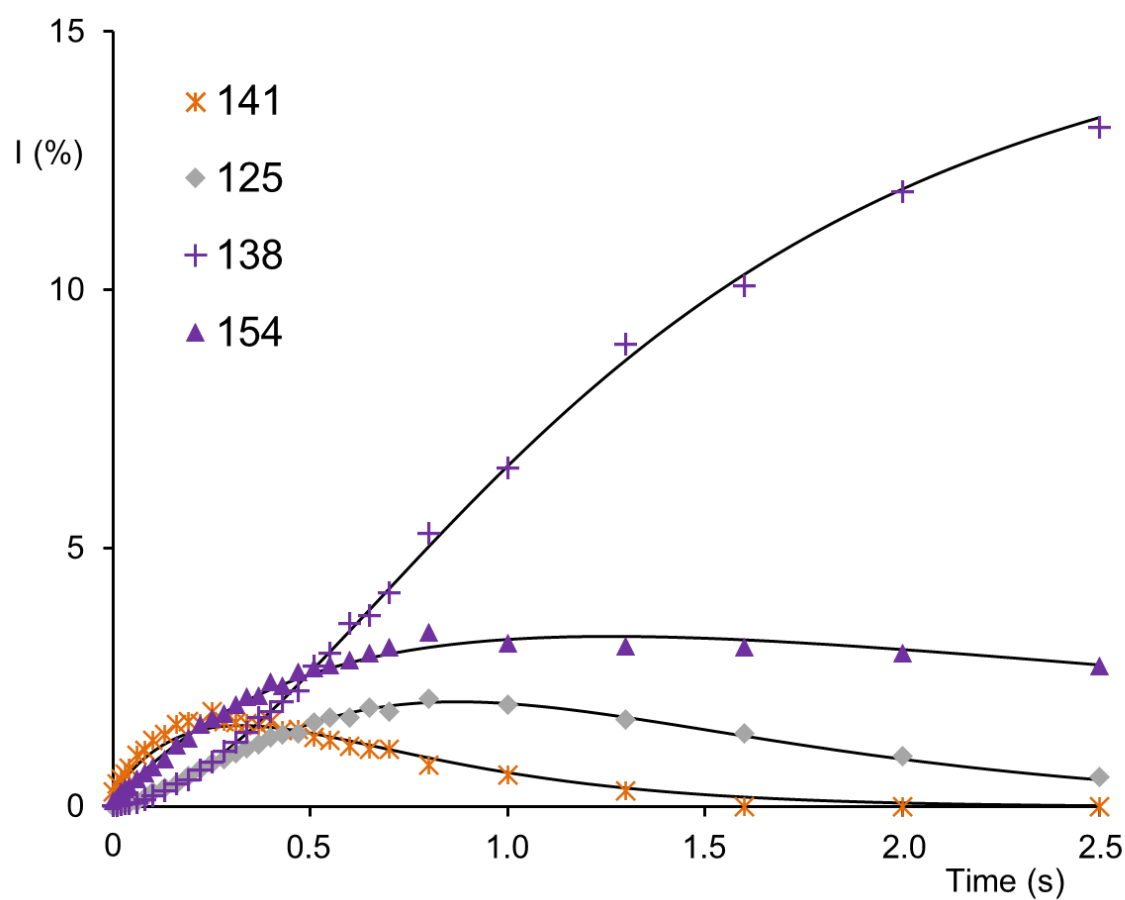


**Figure S9.** IT mass spectrum of the ion-molecule reaction of a)  $[\text{ClO} \cdot \text{Na} \cdot \text{ClO}_2]^-$  product ion at  $m/z$  141 (in red),  $\text{MS}^n$ -isolated from the reaction of  $[\text{ClO}_2 \cdot \text{Na} \cdot \text{ClO}_2]^-$  reactant ion ( $m/z$  157) and b)  $[\text{Cl} \cdot \text{Na} \cdot \text{ClO}_3]^-$  standard ion at  $m/z$  141 (in red), obtained from a 1:1 NaCl/NaClO<sub>3</sub> millimolar solution, towards SO<sub>2</sub> both at an activation time (AT) of 300 ms and a  $P_{\text{SO}_2} = 5.92 \times 10^{-7}$  Torr.

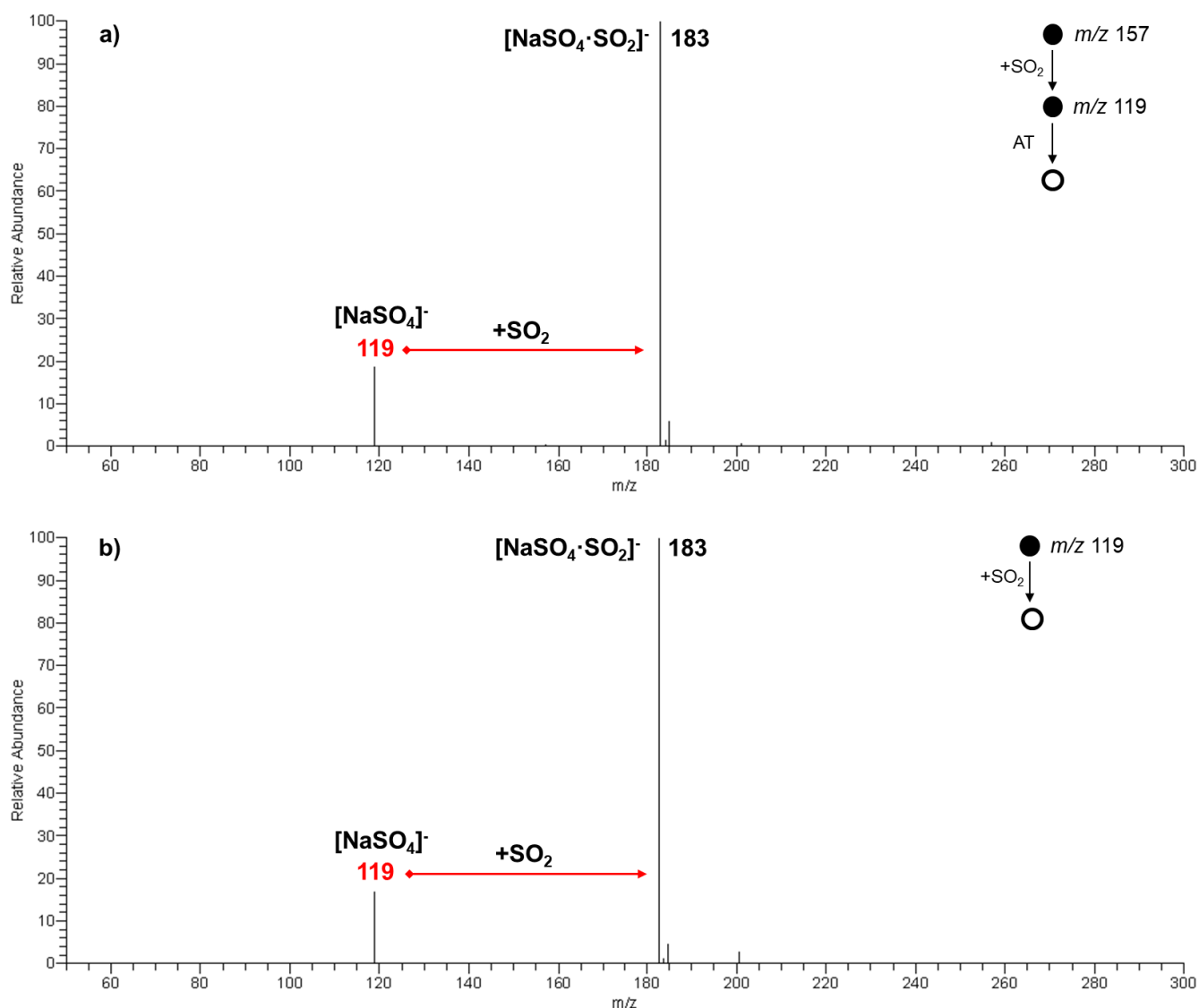




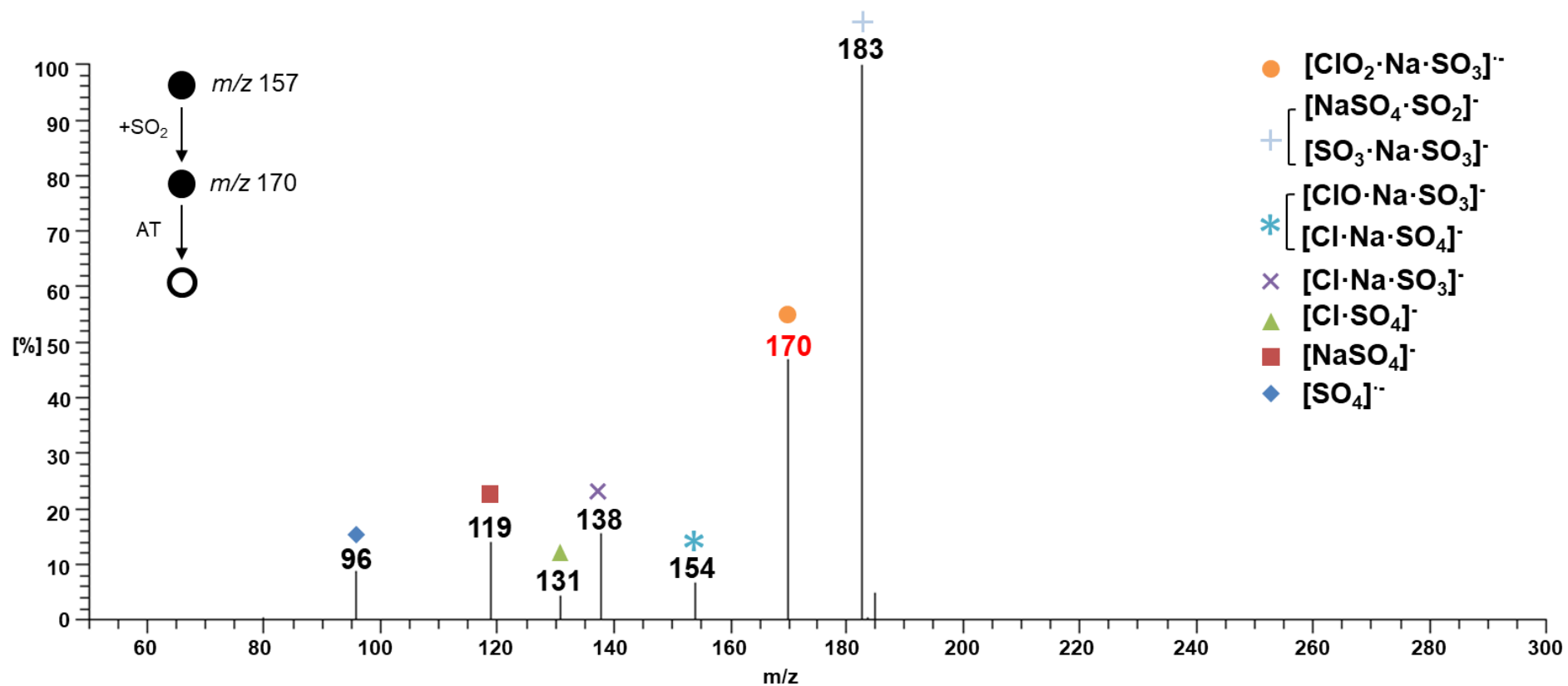
**Figure S10.** IT mass spectrum of the ion-molecule reaction between  $[\text{Cl}\cdot\text{Na}\cdot\text{ClO}_2]^-$  consecutive product ion at  $m/z$  125 (in red),  $\text{MS}^n$ -isolated from the reaction sequence  $m/z$  157  $\rightarrow$   $m/z$  141  $\rightarrow$   $m/z$  125 and  $\text{SO}_2$  at an activation time (AT) of 200 ms and a  $P_{\text{SO}_2} = 5.92 \times 10^{-7}$  Torr.



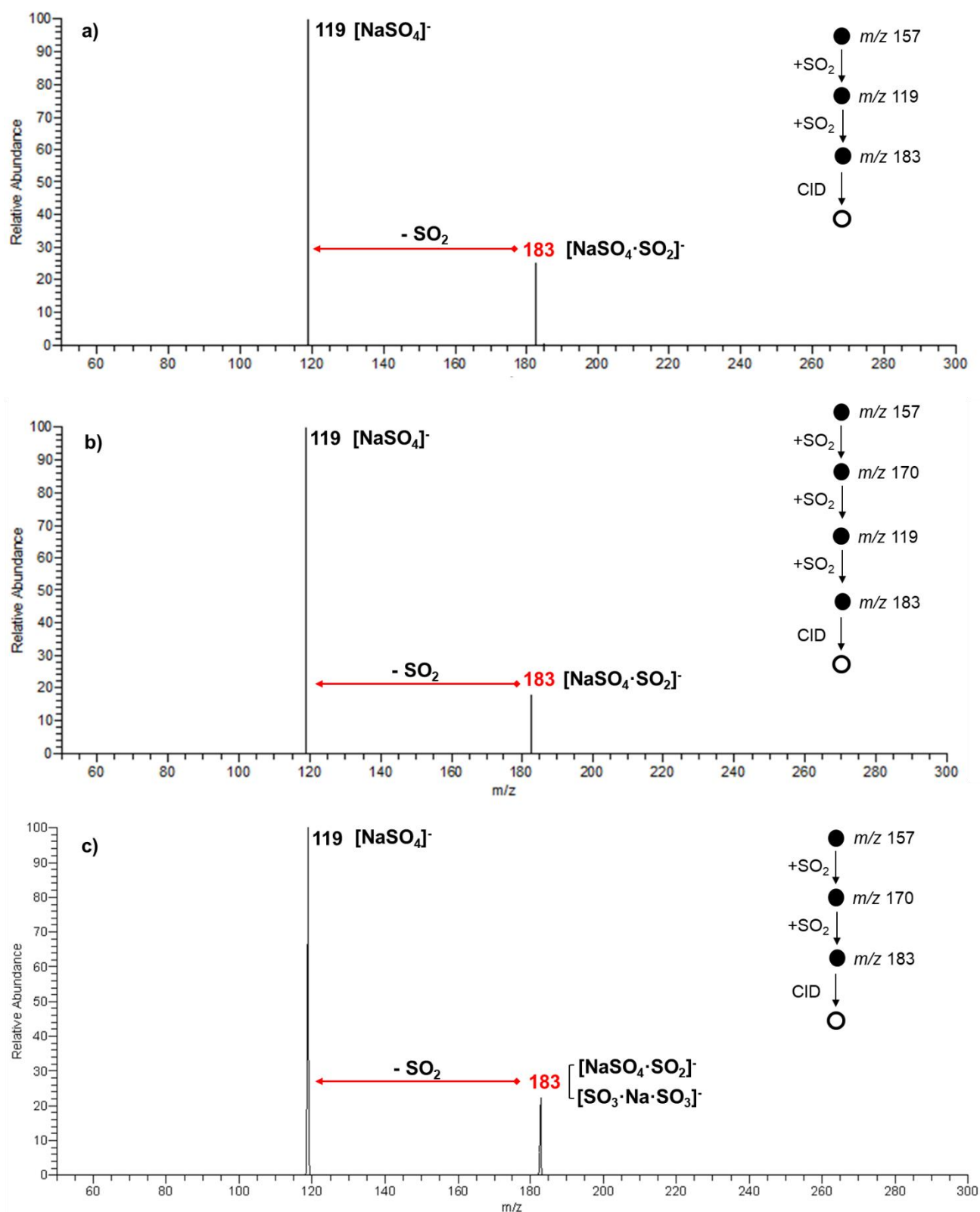
**Figure S11.** Magnified kinetic plot of the reaction of isolated  $[\text{NaClO}_2 \cdot \text{ClO}_2]^-$  ions ( $m/z = 157$ ) with  $\text{SO}_2$  taken from Figure 4. Only the time progress of the low signals corresponding to ions at  $m/z = 154$ , 141, 138 and 125 are shown, related to the sequences:  $157 \rightarrow 170 \rightarrow 154 \rightarrow 138$  and  $141 \rightarrow 125 \rightarrow 138$ .



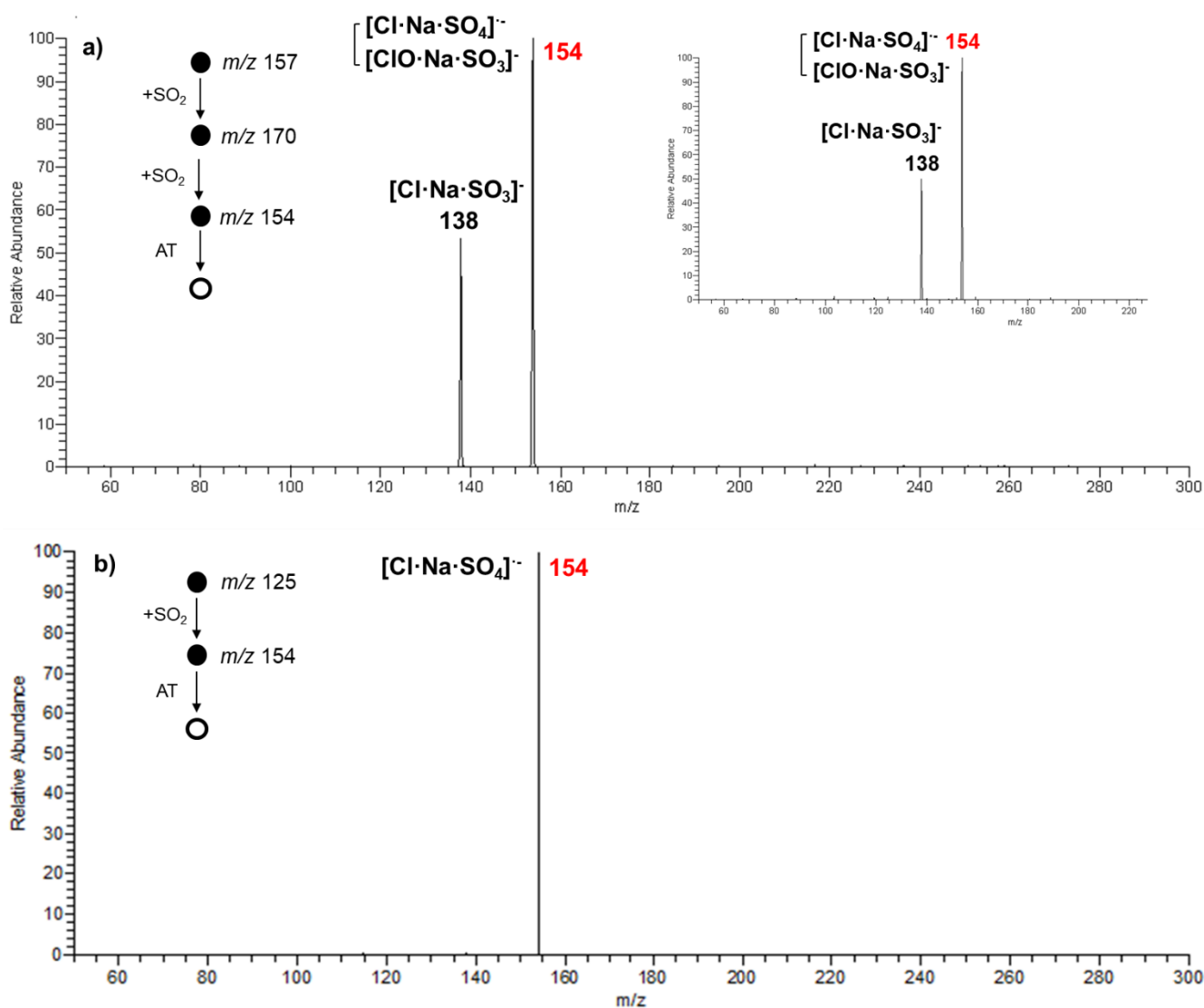
**Figure S12.** IT mass spectrum of the ion-molecule reaction of a)  $[\text{Na} \cdot \text{SO}_4]^-$  product ion at  $m/z$  119 (in red),  $\text{MS}^n$ -isolated from the reaction of  $[\text{ClO}_2 \cdot \text{Na} \cdot \text{ClO}_2]^-$  reactant ion ( $m/z$  157) with  $\text{SO}_2$  ( $P \text{ SO}_2 = 2.30 \times 10^{-7}$  Torr); b)  $[\text{Na} \cdot \text{SO}_4]^-$  standard ion at  $m/z$  119 (in red), obtained from a  $\text{Na}_2\text{SO}_4$  millimolar solution, towards  $\text{SO}_2$  ( $P \text{ SO}_2 = 5.20 \times 10^{-7}$  Torr). Both spectra are acquired with at an activation time (AT) of 5000 ms.



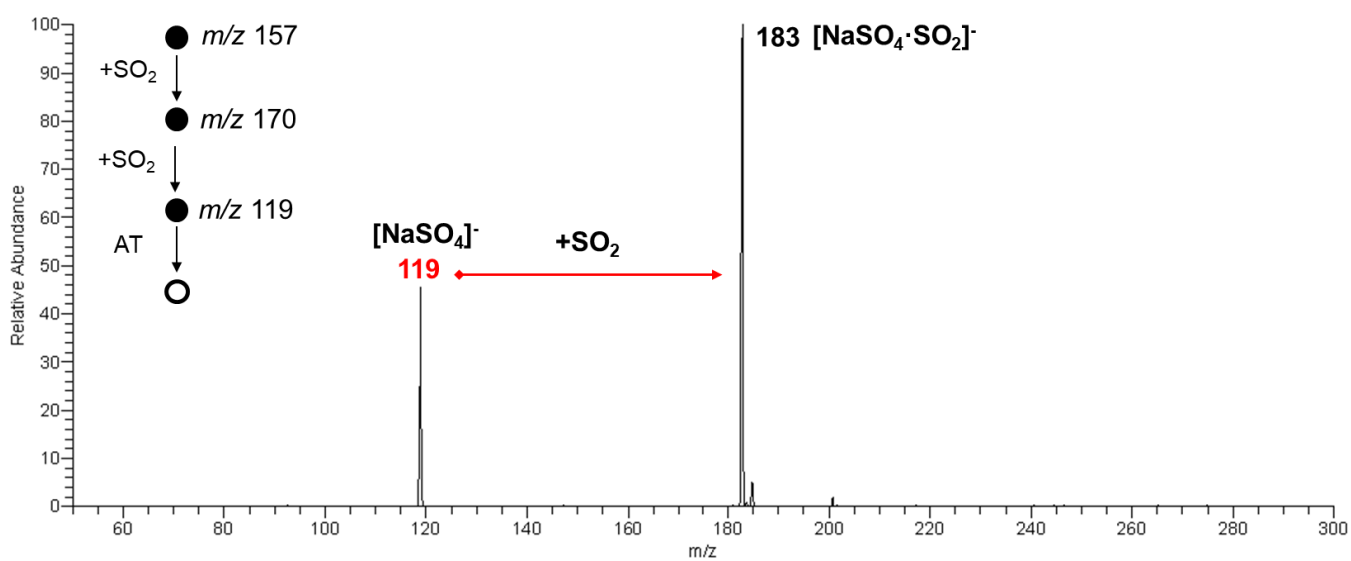
**Figure S13.** IT mass spectrum of the ion-molecule reaction between  $[\text{ClO}_2\cdot\text{Na}\cdot\text{SO}_3]^\cdot$  product ion at  $m/z$  170 (in red)  $\text{MS}^n$ -isolated from the reaction sequence  $m/z$  157  $\rightarrow$   $m/z$  170 and  $\text{SO}_2$  at an activation time (AT) of 700 ms and a  $P \text{ SO}_2 = 1.64 \times 10^{-7}$  Torr.



**Figure S14.** IT-CID mass spectrum of product ion at  $m/z$  183 (in red)  $\text{MS}^n$ -isolated from the reaction sequence a)  $m/z$  157  $\rightarrow$   $m/z$  119  $\rightarrow$   $m/z$  183, b)  $m/z$  157  $\rightarrow$   $m/z$  170  $\rightarrow$   $m/z$  119  $\rightarrow$   $m/z$  183 and  $m/z$  157  $\rightarrow$   $m/z$  170  $\rightarrow$   $m/z$  183.



**Figure S15.** IT mass spectrum of the ion-molecule reaction of a) a mixed ionic population at  $m/z$  154 (in red),  $\text{MS}^n$ -isolated from the reaction sequence  $m/z$  157  $\rightarrow$   $m/z$  170  $\rightarrow$   $m/z$  159 with  $\text{SO}_2$  ( $P_{\text{SO}_2} = 6.25 \times 10^{-7}$  Torr) b)  $[\text{Cl}\cdot\text{Na}\cdot\text{SO}_4]^-$  ion at  $m/z$  154 (in red)  $\text{MS}^n$ -isolated from the reaction of  $[\text{Cl}\cdot\text{Na}\cdot\text{ClO}_2]^-$  reactant ion ( $m/z$  125), towards  $\text{SO}_2$  ( $P_{\text{SO}_2} = 2.30 \times 10^{-7}$  Torr) both at an activation time (AT) of 150 ms. In the inset the AT is 10.000 ms.



**Figure S16.** IT mass spectrum of the ion-molecule reaction between  $[\text{Na} \cdot \text{SO}_4]^-$  product ion at  $m/z$  119 (in red),  $\text{MS}^n$ -isolated from the reaction sequence  $m/z$  157  $\rightarrow$   $m/z$  170  $\rightarrow$   $m/z$  119 and  $\text{SO}_2$  at an activation time (AT) of 1500 ms and a  $P \text{ SO}_2 = 6.25 \times 10^{-7}$  Torr.

