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# The Capability of CI-Orbitrap for Gas-Phase Analysis in Atmospheric Chemistry: A Comparison with the CI-APi-TOF Technique

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1           The capability of CI-Orbitrap for gas-phase analysis in  
2                           atmospheric chemistry:

3           A comparison with the CI-API-TOF technique

4  
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6  
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10

11 **Abstract**

12 Chemical ionization Orbitrap mass spectrometry (CI-Orbitrap) represents a promising new technique  
13 for gas-phase analysis in analytical and atmospheric chemistries mainly due to its very high mass  
14 resolving power. In this work, we performed the first side-by-side comparison between a CI-Orbitrap  
15 and the widely used atmospheric pressure interface time-of-flight mass spectrometry (CI-APi-TOF)  
16 using two different chemical ionization methods, i.e., acetate-ion-based ( $\text{CH}_3\text{COO}^-$ ) and aminium-ion-  
17 based ( $\text{n-C}_3\text{H}_7\text{NH}_3^+$ ) schemes. The capability of the CI-Orbitrap at accurately measuring low  
18 concentrations of gaseous species formed from the oxidation of  $\alpha$ -pinene was explored. Although this  
19 study reveals a lack of linearity of the CI-Orbitrap when measuring product ions at very low  
20 concentrations ( $< 1 \times 10^6$  molecules  $\text{cm}^{-3}$ ), very good agreement between both techniques can be  
21 achieved by applying a newly developed linearity correction. It is experimentally shown that the  
22 correction function is independent of the reagent ion used. Thus, accurate quantification of organic  
23 compounds at concentrations as low as  $1 \times 10^5$  molecules  $\text{cm}^{-3}$  by the CI-Orbitrap can be achieved.  
24 Finally, by means of tandem mass spectrometry, the unique capability of the Orbitrap allows the direct  
25 determination of the binding energy of cluster ions between analyte and reagent ions, that is needed  
26 for the assessment of a chosen ionization scheme.

## 27 **Introduction**

28 Biogenic and anthropogenic activities constantly release a wide variety of volatile organic compounds  
29 (VOCs) into the atmosphere.<sup>1,2</sup> Once emitted, VOC are rapidly oxidized to form oxidized VOCs  
30 (OVOCs) spanning a broad range of chemical formulas, and, thus, volatilities.<sup>1,3,4</sup> As a result, organic  
31 compounds play a key role in the formation of atmospheric aerosol by either condensing onto pre-  
32 existing aerosol particles or by forming new particles.<sup>1,2,5,6</sup> VOC emissions strongly impact  
33 atmospheric chemistry, human health, and Earth's climate. More specifically, a critical starting point in  
34 new particle formation (NPF) and growth is the generation of highly oxygenated multifunctional  
35 organic molecules (HOMs) through a process usually referred to as autoxidation.<sup>7-9</sup> In the course of  
36 the autoxidation process, peroxy (RO<sub>2</sub>) radicals, formed via the oxidation of a VOC, undergo an  
37 intramolecular hydrogen shift reaction, ROO → QOOH, followed by the addition of molecular oxygen  
38 resulting in the formation of a new R'O<sub>2</sub> radical: QOOH + O<sub>2</sub> → OOQOOH (R'O<sub>2</sub>) ("Q" stands for  
39 the organic group "R" after intermolecular H shift). This chain reaction can be repeated, yielding a  
40 broad diversity of products depending on the RO<sub>2</sub> radical termination steps.<sup>8,10-12</sup> As a result, HOMs  
41 can be formed efficiently at high enough yields to consider them as a significant source of condensing,  
42 or, in certain cases, even nucleating, organic components.<sup>6-8,13-15</sup> Finally, RO<sub>2</sub> chemistry not only  
43 controls the formation of HOMs and NPF but also impacts the production of secondary pollutants  
44 including O<sub>3</sub> and NO<sub>2</sub>.<sup>16</sup> While in the last decade major breakthroughs have been achieved within the  
45 field of atmospheric oxidation processes and new particle formation,<sup>6-8,17</sup> a complete understanding of  
46 how VOC oxidation products contribute to new particle and SOA formation remains poorly  
47 constrained. Indeed, gas-phase oxidation processes of biogenic and anthropogenic VOCs yield a  
48 number of oxidized products resulting in extremely complex mixture of oxygenated VOCs (OVOCs).  
49 These span a wide range of chemical formulas, structures, and physicochemical properties and pose a  
50 critical challenge in detecting, quantifying, and characterizing key atmospheric species including RO<sub>2</sub>  
51 radicals and HOMs.

52 Mass spectrometric techniques have recently made enormous improvements in detecting and  
53 quantifying gaseous oxygenated species.<sup>18-20</sup> In particular, chemical ionization mass spectrometry  
54 (CIMS) has emerged as a prevailing tool due to its very low detection limits, good sensitivity, and

55 capability of measuring a wide variety of gaseous organic and inorganic species.<sup>8,10,10,21</sup> Chemical  
56 ionization (CI) is a soft ionization technique where the analyte is ionized via a clustering process with  
57 the reagent ion with minimal fragmentation or via proton transfer processes.<sup>21–24</sup> As part of the rapid  
58 development, multiple reagent ion schemes have been tested over the last few years. Due to the  
59 improvements in sensitivity and/or selectivity, a wide variety of oxygenated species, including RO<sub>2</sub>  
60 radicals and stabilized Criegee intermediates, can now be directly analyzed.<sup>10,11,19,20,25,26</sup> However,  
61 most of the CI mass spectrometers offer a rather limited mass resolving power (i.e., from 2 000 to 14  
62 000), hindering yet a complete and unambiguous identification of the compounds of interest.  
63 Consequently, the presence of multiple overlapping ions leads to significant uncertainties that can only  
64 be partly resolved by computational techniques. To overcome these limitations, we have recently  
65 coupled a high-resolution mass spectrometer (Orbitrap) with a CI source.<sup>30</sup> The CI-Orbitrap combines  
66 the benefits of soft atmospheric pressure ionization with a unique mass resolving power ( $R \geq 140\,000$   
67 at  $m/z$  200). In our first study we demonstrated the applicability of this new analytical method and  
68 evaluated its ability in detecting and characterizing OVOCs formed during the oxidation of two  
69 monoterpenes using nitrate-based (NO<sub>3</sub><sup>-</sup>) CI.<sup>30</sup> Nonetheless, a direct comparison with the widely used  
70 atmospheric pressure interface time-of-flight mass spectrometry (CI-APi-TOF) has not been  
71 performed hitherto. Hence, the sensitivity as well as the linearity of the CI-Orbitrap with different  
72 reagent ions operated in the positive or negative mode need to be determined and compared to those of  
73 the CI-APi-TOF.

74         Within the present study, we performed the first side-by-side comparison between a CI-  
75 Orbitrap and a CI-APi-TOF applying two different chemical ionization schemes i.e., the acetate-ion-  
76 based (CH<sub>3</sub>COO<sup>-</sup>)<sup>10,11</sup> and the aminium-ion-based (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>)<sup>11</sup> product ionization. Unlike our  
77 initial study, we performed our experiments in a free-jet system designed to probe the early stage of a  
78 given reaction. A very short residence time was used as well as very low reactant conversion. As a  
79 result, RO<sub>2</sub> radicals are the main products and experiments are performed within atmospheric reaction  
80 conditions, where bimolecular steps are only important for relatively high RO<sub>2</sub>/ HO<sub>2</sub> levels or in the  
81 presence of high enough concentrations of additives (e.g., NO). Hence, very low concentrations of  
82 RO<sub>2</sub> radicals and OVOCs are produced from the ozone and OH radical initiated oxidation of  $\alpha$ -pinene

83 in order to ascertain the benefit and the limitation of the CI-Orbitrap. We also explored the potential of  
84 the CI-Orbitrap in evaluating the binding energies of RO<sub>2</sub> radicals and OVOCs clustered with acetate  
85 and aminium (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>) by means of tandem mass spectral analyses (MS<sup>2</sup>).

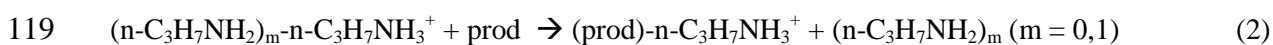
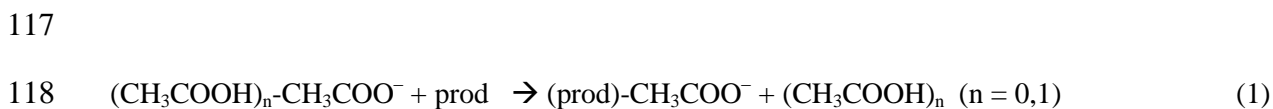
## 86 EXPERIMENTAL SECTION

87 Ozonolysis and OH radical initiated oxidation of  $\alpha$ -pinene (C<sub>10</sub>H<sub>16</sub>) were performed under dry  
88 conditions (RH < 0.1%) in air using a free-jet flow system at a temperature of 297 ± 1 K and  
89 atmospheric pressure.<sup>10,11</sup> This flow system allows the investigation of VOC oxidation under  
90 atmospheric conditions with negligible wall effects and a reaction time of 7.9 s. Ozone produced from  
91 a low-pressure mercury lamp or isopropyl nitrite (IPN) was premixed with air (5 L/min (STP) ) and  
92 injected through the inner tube into the main gas stream (95 L/min (STP)) containing  $\alpha$ -pinene diluted  
93 in air. Ozonolysis experiments (dark reaction) were performed in the absence of an OH scavenger, i.e.,  
94 the in-situ OH radical formation from ozonolysis led to a combined O<sub>3</sub>/OH +  $\alpha$ -pinene reaction. In the  
95 pure OH experiments based on IPN photolysis, 8 NARVA 36W Blacklight Blue lamps were used for  
96 illuminating the flow system. All gas flows were set by means of calibrated gas flow controllers (MKS  
97 1259/1179). The concentration of  $\alpha$ -pinene was maintained at 5.0 × 10<sup>11</sup> molecules cm<sup>-3</sup>, while ozone  
98 and IPN were ramping up from 2.5 × 10<sup>10</sup> to 5.6 × 10<sup>11</sup> and from 1.7 × 10<sup>10</sup> to 6.7 × 10<sup>11</sup> molecules cm<sup>-3</sup>,  
99 respectively.

100 The chemical composition of the oxygenated products was retrieved in real time by a Q-  
101 Exactive Orbitrap Plus mass spectrometer (Thermo Scientific) and a chemical ionization - atmospheric  
102 pressure interface - time-of-flight mass spectrometer (CI-APi-TOF, Tofwerk AG). Both instruments  
103 have been described elsewhere and were equipped with a similar Eisele-type inlet.<sup>21,30-33</sup> While the CI  
104 inlet mounted on the APi-TOF is manufactured by Airmodus (Finland), the CI inlet installed on the  
105 Orbitrap is a home-built version with minor modifications regarding to the commercially available  
106 inlet (i.e., dimensions of the drift tube and specific flange, see for more details ref.<sup>30</sup>). The sample flow  
107 rate for both instruments was set at ~ 10 L/min (STP). Protonated n-propylamine (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>) or  
108 acetate (CH<sub>3</sub>COO<sup>-</sup>) ions were produced using an X-ray source or an Am-241 source for the Orbitrap  
109 and the APi-TOF, respectively. In the ion-molecule-reaction (IMR) zone, the reagent ions from a clean  
110 sheath nitrogen flow were guided into the concentric sample flow by an electrical field without

111 turbulent mixing of both streams. The residence time within the IMR zone was in the range of 200 –  
112 300 ms in both instruments.

113 The reagent ions were  $(\text{CH}_3\text{COOH})_n\text{-CH}_3\text{COO}^-$  ( $n = 0,1$ ) and  $(n\text{-C}_3\text{H}_7\text{NH}_2)_m\text{-n-C}_3\text{H}_7\text{NH}_3^+$  ( $m$   
114  $= 0,1$ ) in the negative and positive mode, respectively.  $\text{RO}_2$  radicals as well as closed-shell products,  
115 called “prod” for all together, were detected as clusters with the respective reagent ions according to  
116 the following reactions (1) and (2):



120

121 It is important to mention that the absolute calibration of the detected oxygenated products is  
122 impossible due to a lack of authentic reference substances for  $\text{RO}_2$  radicals and the majority of closed-  
123 shell products. Thus, the product signals of both mass spectrometers were normalized to the sum of  
124 the reagent ions, i.e.,  $\Sigma[(\text{CH}_3\text{COOH})_n\text{-CH}_3\text{COO}^- (n = 0,1)]$  or  $\Sigma[(n\text{-C}_3\text{H}_7\text{NH}_2)_m\text{-n-C}_3\text{H}_7\text{NH}_3^+ (m =$   
125  $0,1)]$ . The resulting normalized signals were used for the comparison in order to evaluate the  
126 performance of both techniques.

127 However, the lower end value of the calibration factor  $f$  can be calculated considering the ion-  
128 molecule reaction within the CI-inlet,  $f = 1 / (k \times t \times f_{\text{inlet}})$ ,<sup>34</sup> where  $k$  is the rate coefficient of the ion-  
129 molecule reaction,  $t$  the reaction time and  $f_{\text{inlet}}$  corresponds to the “prod” loss in the sampling tube.  
130 Diffusion loss of the  $\text{RO}_2$  radicals and OVOCs in the sampling lines to the CI-API-TOF and the CI-  
131 Orbitrap were calculated to be 12% and 38%, respectively, assuming diffusion-controlled wall  
132 losses.<sup>10</sup> Taking into account this diffusion loss,  $f_{\text{inlet}} = 0.88$ , and a reaction time of the ion-molecule  
133 reaction  $t = 0.2 - 0.3$  s (which is similar for both instruments), a calibration of  $f_{\text{calc}} = (1.3 - 2.8) \times 10^9$   
134 molecules  $\text{cm}^{-3}$  can be calculated. It should be mentioned that using the only reliable absolute  
135 calibration technique (i.e., sulfuric acid) a calibration factor of  $f_{\text{H}_2\text{SO}_4,\text{exp}} = 1.85 \times 10^9$  molecules  $\text{cm}^{-3}$   
136 was determined in previous experiments. This value is in good agreement with the range of  $f_{\text{calc}}$ . The  
137 calibration factor  $f$  of reactions (1) and (2) was set equal to  $f_{\text{H}_2\text{SO}_4,\text{exp}}$  by practical reasons. The

138 uncertainty of the lower end “prod” concentrations determined according to equation (1) or (2) is  
139 assumed to be not higher than a factor of two due to the expected uncertainty of the used calibration  
140 factor  $f_{\text{H}_2\text{SO}_4, \text{exp}} = 1.85 \times 10^9$  molecules  $\text{cm}^{-3}$ , and possible inaccuracy connected with the duty cycle  
141 correction. Therefore, only lower limit product concentrations are available based on this calculated  
142 calibration factor.

143 Duty cycle correction was applied for the APi-TOF data in order to account for the  $m/z$   
144 discrimination during the ion extraction.<sup>10,24,35</sup> In the case of the CI-Orbitrap, for each experiment, the  
145 ion transmission was evaluated by comparing the loss of the number of charges of the reagent ions  
146 with the increase of the number of charges of all the ions within the  $m/z$  200 – 600 Th. This simple  
147 method provides a rough estimate of the ion transmission for the compounds of interest relative to the  
148 reagent ions. As a result, a factor of 2 was applied to correct for the lower ion transmission of the  
149 reagent ions in order to determine the normalized signals.

150 In addition, we further evaluated the ion transmission of the Q Exactive Orbitrap in the  $m/z$  53  
151 – 800 Th using the depletion method described by Heinritzi et al.<sup>36</sup> This method takes into  
152 consideration losses within the inlet as well as the different ion optics and C-Trap (see Figure S1). In  
153 short, 4 different perfluorinated acids were introduced into the mass analyzer in order to deplete the  
154 reagent ions. As a result, the relative transmission efficiency can be obtained by comparing the  
155 decrease of signal strength of the reagent ions with the rising signals from the perfluorinated acids at  
156 larger masses (see supplementary information for more details). The relative ion transmission was  
157 only determined for the Q-Exactive Orbitrap using nitrate-ion based chemistry. It should be pointed  
158 out that the depletion method leads to significantly different results for the ion transmission of a mass  
159 spectrometer than absolute calibration methods.<sup>7,36-38</sup> Nevertheless, the results of the depletion method  
160 provide a first insight into the ion transmission of a Q Exactive Orbitrap.

161 The Q Exactive Plus Orbitrap (Orbitrap-Tropos) was used in positive (i.e.,  $\text{n-C}_3\text{H}_7\text{NH}_3^+$ ) and  
162 negative mode (i.e.,  $\text{CH}_3\text{COO}^-$ ) and connected to the free-jet flow system. The Q Exactive Orbitrap  
163 (Orbitrap-IRCELYON) was solely used in negative mode ( $\text{NO}_3^-$ ) to determine the ion transmission  
164 and to developed the linearity correction. Both instruments were operated using the same settings and  
165 were run in full scan mode with a high mass resolving power of 140 000 (at  $m/z$  200 Th), allowing an



166 identification of a wide variety of species. The instruments were operated in negative or positive  
167 mode, scanning from  $m/z$  50 to 750 Th with an automatic gain control (AGC) target of  $1 \times 10^5$   
168 charges, a maximum injection time of 1 s, resulting in a scan rate of 0.2 scans/s. Spectra were  
169 averaged of 5 microscans (1 microscan corresponding to 1 ion injection). The stacked-ring ion guide  
170 (or S-Lens) is a radio frequency (RF) device efficiently capturing and focusing the ions into a tight  
171 beam. As previously described it contains a series of electrodes where voltages are applied in order to  
172 focus the ions. The S-lens level was maintained at 60%, to maximize ion transmission and the limit of  
173 detection. The C-Trap consist of a RF-based ion collecting trap (Figure S1), which is automatically  
174 controlled by the AGC (automatic gain control) in order to prevent space-charge effects. In order to  
175 evaluate the impact of the number of charges collected in the C-trap, the AGC target of the Orbitrap-  
176 Tropos instrument was scanned from  $5 \times 10^4$  to  $1 \times 10^6$  charges. External mass calibrations were  
177 performed prior to the experiments by injecting a 2 mM sodium acetate solution using an electrospray  
178 ionization source. This procedure provided a suite of negative and positive adduct ions in the desired  
179 mass range of  $m/z$  59 – 700 Th. Tandem mass spectral ( $MS^2$ ) analyses were performed by ramping up  
180 the normalized collision energy (NCE) from 1 – 7 eV (i.e., normalized to singly charged ions at  $m/z$   
181 500). Thus, to retrieve the collision energy (CE) encountered by ions at any given  $m/z$  ratio within the  
182 higher-energy collision dissociation (HCD) cell, the CE can be calculated as follows:  $CE = (m/z / 500)$   
183  $\times$  NCE  $\times$  f, where f stands for the number of charges of the ion. To ensure an optimal detection of the  
184 product ions, the mass spectra obtained using the CI-APi-TOF and the CI-Orbitrap were averaged over  
185 10 minutes each. A time resolution of 5 min was used for the  $MS^2$  analyses conducted by the Orbitrap.  
186 The high-resolution Orbitrap data were analyzed by XCalibur 4.1 (Thermo Scientific) software  
187 package to determine accurate composition and the abundance of the compounds of interest. Peak  
188 fitting of the CI-APi-TOF data was performed by means of the Matlab-based toftools software.<sup>37</sup>

189

## 190 RESULTS AND DISCUSSION

191 **Characterization of the CI-Orbitrap.** Despite the wealth of studies using the Orbitrap technique,  
192 little is known about the capability of the Orbitrap in measuring compounds on-line at low  
193 concentrations. For example it has been reported that the Orbitrap can provide a non-linear response,

194 potentially impacting isotope ratios, determination and the quantification of compounds present at  
195 extremely low concentrations.<sup>39</sup> In view of these findings available from literature, we evaluated the  
196 performance of the CI-Orbitrap by comparing the measured vs. the theoretical isotopic intensities  
197 using product ions analyzed by the Orbitrap-Tropos using protonated n-propylamine ( $n\text{-C}_3\text{H}_7\text{NH}_3^+$ )  
198 and acetate ( $\text{CH}_3\text{COO}^-$ ). To further estimate the impact of different reagent ions, results from our  
199 former study performed with the Orbitrap-IRCELYON using nitrate-ion based chemistry<sup>30</sup> are also  
200 compared here. In both cases, OVOCs were continuously generated in the flow tube from either the  
201 ozonolysis and/or OH radical initiated oxidation of  $\alpha$ -pinene. Hence, the abundance of the main  
202 OVOCs (e.g.,  $\text{C}_{10}\text{H}_{14,16}\text{O}_x$ ;  $\text{C}_{20}\text{H}_{30,32}\text{O}_x$ ) and  $\text{RO}_2$  radicals (e.g.,  $\text{C}_{10}\text{H}_{15,17}\text{O}_x$ ) at nominal masses  $M$ , ( $M$   
203  $+ 1$ ) and ( $M + 2$ ), corresponding to their  $^{13}\text{C}$  atom and  $^{18}\text{O}$  atom fraction, were measured to cover a  
204 wide range of normalized product signals in the range of  $5 \times 10^{-7}$  to  $5 \times 10^{-2}$ . Signal intensities  
205 reported in Figure 1A were obtained with an AGC target of  $1 \times 10^5$  charges. As depicted in Figure 1A,  
206 when the ratio is equal to 1.0 for normalized signal  $> \sim 4 \times 10^{-4}$  to ( $\sim 1 \times 10^6$  molecules  $\text{cm}^{-3}$ ), the  
207 Orbitrap is providing a linear measure of the ion intensity. However, this ratio dropped significantly  
208 for normalized signals below  $\sim 4 \times 10^{-4}$ . Such a situation occurs when the ion intensity is close to the  
209 instrumental threshold, i.e., by using standard settings the Orbitrap mass analyzer records only signals  
210 if  $S/N > 1.3$ . The ion signals below this threshold are treated as undetected by the acquisition software.  
211 Due to the statistics, peaks with an average  $S/N = 1.5$  for example will appear above this threshold  
212 only in a limited amount of cases reducing the resulting peak intensity.<sup>40</sup> As a result, for a normalized  
213 signal smaller than  $1 \times 10^{-5}$ , the CI-Orbitrap only detects 5 – 10 % of the “true ion number  
214 distribution”. That means, using the instrumental parameters and the calibration factor employed here  
215 ( $1.85 \times 10^9$  molecules  $\text{cm}^{-3}$ ) the limit of quantification (LoQ, corresponding to lowest normalized  
216 signal observed within the linear range) of the Orbitrap was evaluated to be  $\sim 1 \times 10^6$  molecules  $\text{cm}^{-3}$   
217 at a 10-minute integration time. It is worth pointing out that the limit of detection (LoD, corresponding  
218 to the lowest normalized signal observed) is likely one or two orders of magnitude lower than the LoQ  
219 but due to the lack of linearity accurate numbers cannot be directly provided. By adjusting the AGC  
220 target the linear range can be shifted towards lower ion concentrations as shown in Figure 1B. This  
221 can be explained by larger number of ions trapped within the C-trap prior to the Orbitrap scan

222 resulting in more ions entering the Orbitrap mass analyzer. This leads to an enhanced S/N ratio and  
223 better statistics. Hence, we have evaluated the impact of the AGC target (scanned from  $5 \times 10^4$  to  $1 \times$   
224  $10^6$  charges) on the linearity and found that by optimizing the AGC target, the LoQ of the CI-Orbitrap  
225 is anticipated to be greatly extended. However, as most of our previous experiments were performed  
226 using an AGC target of  $1 \times 10^5$  charges, we kept this setting to perform the side-by-side comparison.

227 **Comparison CI-Orbitrap vs CI-APi-TOF.** To evaluate the performance of the CI-Orbitrap  
228 compared to the widely used CI-APi-TOF technique we directly performed side-by-side experiments.  
229 Both instruments, equipped with a similar type of inlet originally designed by Eisele et al.<sup>31</sup> and  
230 running with the same reagent ion, sampled concurrently RO<sub>2</sub> radicals as well as OVOCs produced  
231 under well-controlled reaction conditions. We focused on the detection of RO<sub>2</sub> radicals produced from  
232 the oxidation of  $\alpha$ -pinene. Using acetate and aminium ( $n\text{-C}_3\text{H}_7\text{NH}_3^+$ ) as the reagent ions, the main RO<sub>2</sub>  
233 radicals from  $\alpha$ -pinene oxidation, HO-C<sub>10</sub>H<sub>16</sub>(O<sub>2</sub>) <sub>$\alpha$</sub> O<sub>2</sub> ( $\alpha = 0, 1, 2$ ), were detected by means of the CI-  
234 Orbitrap, in line with the findings of the CI-APi-TOF.<sup>24,30,35</sup> As depicted in Figures 2 and S2, the mass  
235 resolving power of the Orbitrap can accurately distinguish the different species, which is often  
236 impossible with typical TOF mass analyzers. To further illustrate the difference, we have directly  
237 compared ion signals measured by the CI-Orbitrap and by the CI-APi-TOF equipped with a high  
238 resolution mass analyzer (HR-TOF, resolution  $\sim 3000$ ) (Figure 2).

239 Figure 3 shows the results of the OH radical-initiated oxidation of  $\alpha$ -pinene. The OH radicals  
240 were generated by isopropyl nitrite (IPN) photolysis. The formation of the additional RO<sub>2</sub> radical HO-  
241 C<sub>10</sub>H<sub>15</sub>(OH)(O<sub>2</sub>)O<sub>2</sub> can be explained by the reaction of HO-C<sub>10</sub>H<sub>16</sub>(O<sub>2</sub>)<sub>2</sub>O<sub>2</sub> with NO and subsequent  
242 radical isomerization as discussed in a former study.<sup>35</sup> NO is formed from the IPN photolysis. In  
243 addition to the RO<sub>2</sub> radicals, also closed-shell products were detected including carbonyls and organic  
244 nitrates produced from the RO<sub>2</sub> + NO reactions.<sup>16</sup> Lastly, products arising from other bimolecular RO<sub>2</sub>  
245 reactions were not detected or were below the detection limit under the selected experimental  
246 conditions due to the relatively low RO<sub>2</sub> radical concentrations  $< 10^8$  molecules cm<sup>-3</sup> and the very  
247 short reaction time of 7.9 s.

248 As shown in Figure 3, for uncorrected normalized intensities above  $(2 - 3) \times 10^{-4}$   
249 (corresponding to  $\sim (4 - 6) \times 10^5$  molecules cm<sup>-3</sup>) both techniques are in very good agreement. The lack

250 of linearity hampers the Orbitrap, unlike the APi-TOF, to accurately measure lower concentrations.  
251 However, this lack of linearity appears to be independent of the instrument and the type of reagent  
252 ions (Figure 1A). This behavior indicates that this instrumental limitation can be overcome in order to  
253 retrieve the “correct” signal strength for peaks with lowest signal intensity. Indeed, using all  
254 measurements from multiple experiments and reagent ions, a function named “sigmoidal correction  
255 function” based on a fitting algorithm using a characteristic sigmoidal shape can be determined.  
256 Therefore, raw normalized signals (corrected for sampling losses) measured with the CI-Orbitrap were  
257 further corrected using the “sigmoidal correction function”, see also Figure 1. By applying this  
258 method, all the data were corrected (open markers), which greatly helps maintaining the good  
259 agreement between both techniques (Figure 3). However, for uncorrected signal intensities below a  
260 threshold of  $5 \times 10^{-6} - 1 \times 10^{-5}$  this approach results in an overestimation of the ion concentrations as  
261 the signal is likely very close to the noise level of the instrument. As a result, such data points were  
262 not included in Figures 3, 4, S3 and S4. While the APi-TOF can further help correcting this lack of  
263 linearity we preferred to propose a method based only on the signal acquired by the Orbitrap. Hence,  
264 the reported LoD is likely an upper limit and might be even pushed further with appropriate and  
265 collocated instrumentations.

266 Overall, product signals measured by CI-Orbitrap and the CI-APi-TOF are mostly within a  
267 factor of 2 (Figure 5) providing a good agreement between these two analytical techniques for  
268 corrected normalized signal intensity ranging from  $\sim 5 \times 10^{-5}$  to  $1 \times 10^{-2}$  (corresponding to  $\sim 1 \times 10^5$  to  
269  $2 \times 10^7$  molecules  $\text{cm}^{-3}$ ). Exception are the measurements of highly oxidized products using acetate  
270 ionization. The reason for that is not clear at the moment. It is worth pointing out that the positive  
271 mode measurements were less impacted by the lack of linearity compared to negative mode  
272 measurements. This is explained by the fact that at a given product concentration, the resulting ion  
273 intensity measured by aminium ( $\text{n-C}_3\text{H}_7\text{NH}_3^+$ ) ionization is much greater than for acetate ionization. In  
274 the case of the highest oxidized  $\text{RO}_2$  radicals, i.e.,  $\text{HO-C}_{10}\text{H}_{16}(\text{O}_2)_2\text{O}_2$  and  $\text{HO-C}_{10}\text{H}_{15}(\text{OH})(\text{O}_2)\text{O}_2$   
275 bearing -OH and -OOH moieties, the obtained corrected signal intensities are almost identical within a  
276 factor of two applying either acetate or aminium ( $\text{n-C}_3\text{H}_7\text{NH}_3^+$ ) for product ionization. This fact is  
277 obviously due to strong binding of these  $\text{RO}_2$  radicals to both reagent ions. Thus, a near-maximum

278 detection sensitivity can be expected for these reagent ions.<sup>41,42</sup> On the other hand, for the less oxidized  
279 RO<sub>2</sub> radicals HO-C<sub>10</sub>H<sub>16</sub>O<sub>2</sub> and HO-C<sub>10</sub>H<sub>16</sub>(O<sub>2</sub>)O<sub>2</sub> the detection sensitivity based on aminium (n-  
280 C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>) ionization is definitely higher compared to acetate ionization, i.e., by a factor of 500 –  
281 1000 in the case of HO-C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>.<sup>42</sup>

282 Ozonolysis experiments in the absence of an OH scavenger were conducted in order to  
283 generate a larger variety of products, mainly RO<sub>2</sub> radicals, formed from the simultaneous ozone and  
284 OH radical reactions of  $\alpha$ -pinene. Accordingly, two types of RO<sub>2</sub> radicals have been formed, i.e., the  
285 ozonolysis-derived RO<sub>2</sub> radicals O<sub>2</sub>O-C<sub>10</sub>H<sub>15</sub>(O<sub>2</sub>)<sub>x</sub>O<sub>2</sub> (x = 0, 1, 2, 3) and the OH-derived RO<sub>2</sub> radicals  
286 HO-C<sub>10</sub>H<sub>16</sub>(O<sub>2</sub>) <sub>$\alpha$</sub> O<sub>2</sub> ( $\alpha$  = 0, 1, 2).<sup>7,35</sup> Figure 4 presents the signal intensities of both types of RO<sub>2</sub>  
287 radicals measured by means of aminium (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>) ionization. While the agreement for the most  
288 oxidized RO<sub>2</sub> radicals is again very good, the signals of the less oxidized species O<sub>2</sub>O-C<sub>10</sub>H<sub>15</sub>O<sub>2</sub> and  
289 HO-C<sub>10</sub>H<sub>16</sub>O<sub>2</sub> (Figures 3 and 4) are systematically higher using the CI-Orbitrap by a factor of two or  
290 higher. In contrast, for the most oxidized RO<sub>2</sub> the difference between the two instruments was only ~  
291 20%. Such a disparity might be explained by less efficient declustering of the relatively weakly bound  
292 aminium clusters of O<sub>2</sub>O-C<sub>10</sub>H<sub>15</sub>O<sub>2</sub> and HO-C<sub>10</sub>H<sub>16</sub>O<sub>2</sub> in the CI-Orbitrap compared to the CI-API-TOF.  
293 This results in a more sensitive detection of the initially formed RO<sub>2</sub> radicals with relatively low  
294 oxygen content. It is important to mention that by applying the transmission curve to the CI-Orbitrap  
295 data, a larger discrepancy exist between the results of both instruments, see Figure S6. This  
296 discrepancy is obviously due to the different ion transmission corrections. Indeed, using the  
297 parameters selected in this study the ion transmission within the Orbitrap exhibit a steep increase  
298 between from  $m/z$  60 to 300 Th (SI). However, much more experimental effort is needed in the future  
299 for a reliable determination of the ion transmission of both instruments and for different reagent ions.  
300 Hence it would be possible to determine i) how good the duty cycle correction accounts for the overall  
301 ion transmission of the CI-API-TOF and ii) what is the accuracy of the depletion methods in  
302 comparison to absolute calibration methods.

303 Overall, the side-by-side comparison displays a very good agreement of the results of the CI-  
304 Orbitrap and the CI-API-TOF with the exception of the lowest oxidized reaction products. By using  
305 the “sigmoidal correction function”,  $1.85 \times 10^9$  molecules cm<sup>-3</sup> as the calibration factor for an AGC

306 target of  $1 \times 10^5$  charges, the LoQ of the CI-Orbitrap can be as low as  $1 \times 10^5$  molecules  $\text{cm}^{-3}$  at a 10-  
307 minute integration time.

308 **Determination of cluster binding energy.** In common CI-APi-TOF approaches, the organic  
309 molecules of interest are observed as molecular clusters with the reagent ion (e.g., with  $\text{CH}_3\text{COO}^-$  or  
310  $n\text{-C}_3\text{H}_7\text{NH}_3^+$ ), see also eq. (1) and (2). In order to provide an accurate quantification of the compounds  
311 of interest it is essential to constrain the sensitivity of the reagent ion to OVOCs. To reach this goal,  
312 characterizing any limitations when detecting the compounds of interest, including the ion–molecule  
313 collision limit and the ion–molecule reaction time is critical. The proficiency of any neutral molecule  
314 to bind to the reagent ion is directly linked to the binding energy of the adduct.

315 Accordingly, a weakly bound adduct can undergo declustering, i.e., collision-induced  
316 dissociation (CID), during the flight through the mass analyzer. Ultimately, the binding energy of the  
317 adduct and the energy of the collisions with gas molecules in the mass spectrometer will define the  
318 survival probability of the adduct ions. To constrain this parameter, procedures based on CID  
319 measurement coupled to quantum chemical methods have been proposed to investigate the behavior of  
320 adducts at different collision energies.<sup>43,44</sup> Nonetheless, carrying out such measurements is challenging  
321 for the hundreds of different molecular ions, typically observed with a CI-APi-TOF, especially when  
322 molecular structures remain unknown and/or are highly complex. Therefore, to quantitatively  
323 constrain the effective binding energies of a wide range of OVOCs and  $\text{RO}_2$  radicals, we employed the  
324 capability of the Orbitrap analyzer to perform untargeted  $\text{MS}^2$  analyses. Hence, all ions were injected  
325 into the HCD cell, where they collide at a defined collision energy with  $\text{N}_2$  molecules. The NCE was  
326 ramped up from 1 to 7 eV. During the declustering scans, all potentials upstream the HCD cell  
327 remained identical and only the NCE within the HCD cell incremented, thereby avoiding any changes  
328 in the ion transmission of the mass spectrometer.

329 An example of the declustering analysis is presented in Figure 6A for a set of typical oxidation  
330 products, for which the remaining fraction of individual ions is plotted as a function of the CE  
331 (retrieve for each ion based on their  $m/z$ ). Following the approach previously proposed for iodide-  
332 based clusters,<sup>43–45</sup> a sigmoidal fit was applied to the acquired data (Figure S7), in order to obtain the  
333 following parameters: i) the collision energy at which half of the signal is removed ( $\text{CE}_{50}$ ), and ii) the

334 maximum amplitude of the sigmoidal function ( $S_0$ ), corresponding to the relative signal intensity that  
335 would be measured in absence of declustering processes during the transmission through the mass  
336 spectrometer. In Table S1, the  $CE_{50}$  values of the OH-derived OVOCs and OH-derived  $RO_2$  produced  
337 from the OH radical-initiated oxidation of  $\alpha$ -pinene are reported. While direct comparison with  
338 quantum chemical calculations is not directly possible due to the absence of information on the studied  
339 OVOCs, earlier studies indicate that the values reported in Table S1 are within a fairly good  
340 agreement for binding energies determined for isoprene-derived oxidation products measured with CI-  
341 APiTOF using protonated n-propylamine or acetate.<sup>41,42</sup> For example, Berndt et al.<sup>42</sup> have estimated  
342 binding energies of the HPALD-(n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>) cluster (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) cluster and HPALD-CH<sub>3</sub>COO<sup>-</sup>  
343 cluster of 28.5 and 31.9 kcal mol<sup>-1</sup>, respectively, which is close to the values determined for OVOCs  
344 and  $RO_2$  radicals containing 3 oxygen atoms (Table S1) within this present study.

345         Following the method proposed in former studies,<sup>43,44</sup> we found that the maximum possible  
346 transmission for each compound clustered with protonated n-propylamine (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>) is reached at  
347 a binding energy of  $\sim 35$  kcal mol<sup>-1</sup>. This indicates that for cluster ions having a greater binding  
348 energy, the stability of the adduct will be sufficient to transit through the different ion optics without  
349 significant declustering losses. These results are in line with the side-by-side comparison, where the  
350 largest discrepancy is observed for the lowest oxygenated species (e.g., O,O-C<sub>10</sub>H<sub>15</sub>O<sub>2</sub>; HO-C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>),  
351 i.e., the compounds with the lowest binding energy (Table S1). By optimizing the different voltages,  
352 the declustering processes occurring within the APi-TOF and/or within the Orbitrap can be reduced.  
353 Finally, it is interesting to note that earlier work, performing CID experiments using iodide-based  
354 chemistry, determined a similar threshold, i.e.,  $\sim 30$  kcal mol<sup>-1</sup>.<sup>44</sup>

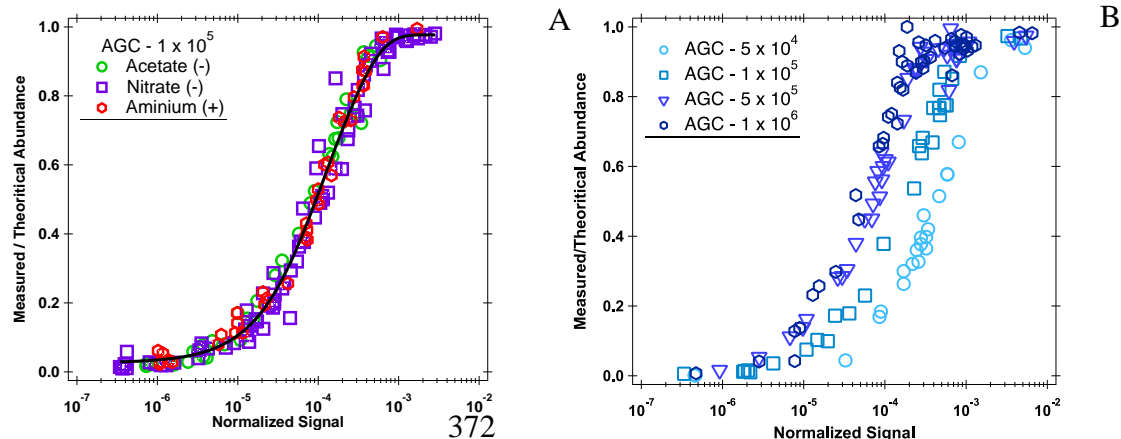
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## 356 CONCLUSIONS

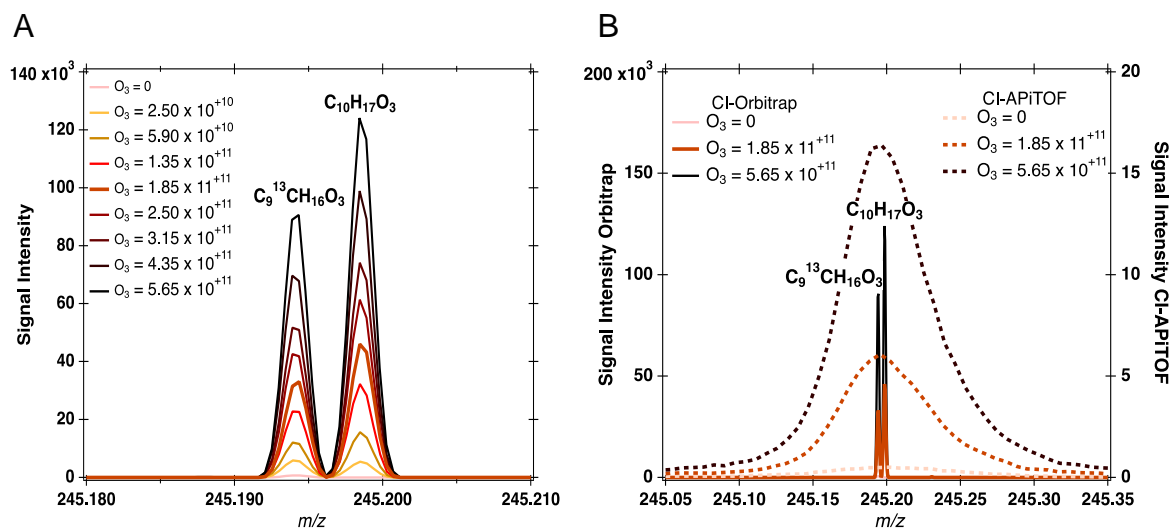
357 In this work, we demonstrated the capability of the CI-Orbitrap in measuring  $RO_2$  radicals as well as  
358 OVOCs at atmospherically relevant concentrations and compared them to simultaneous CI-APi-TOF  
359 measurements. We explored the current limitations of this new analytical technique and demonstrated  
360 that these can be partially overcome through a careful determination of a sigmoidal correction  
361 function. In addition, to unambiguously identify OVOCs formed in the gas phase, the analysis by

362 means of the CI-Orbitrap is able to accurately quantify organic species at concentration down to  $1 \times$   
363  $10^5$  molecules  $\text{cm}^{-3}$ . This LoQ is  $\sim$  one order of magnitude higher in comparison to the APi-TOF used  
364 in this study. In addition to the much greater mass resolving power, another clear advantage over the  
365 APi-TOF technique is the capability of performing  $\text{MS}^2$  analyses needed to retrieve information on the  
366 chemical structure of the compounds of interest and to determine the binding energy of the clusters.  
367 Overall, the combination of high-mass resolving power of the Orbitrap and high sensitivity of the  
368 aminium/ammonium CI represents a powerful analytical tool that can improve our current knowledge  
369 regarding the complexity of the atmospheric gaseous composition. Thus, this new technique can help  
370 to answer some of the questions that so far were unable to be answered due to the pre-existing  
371 instrument limitations.



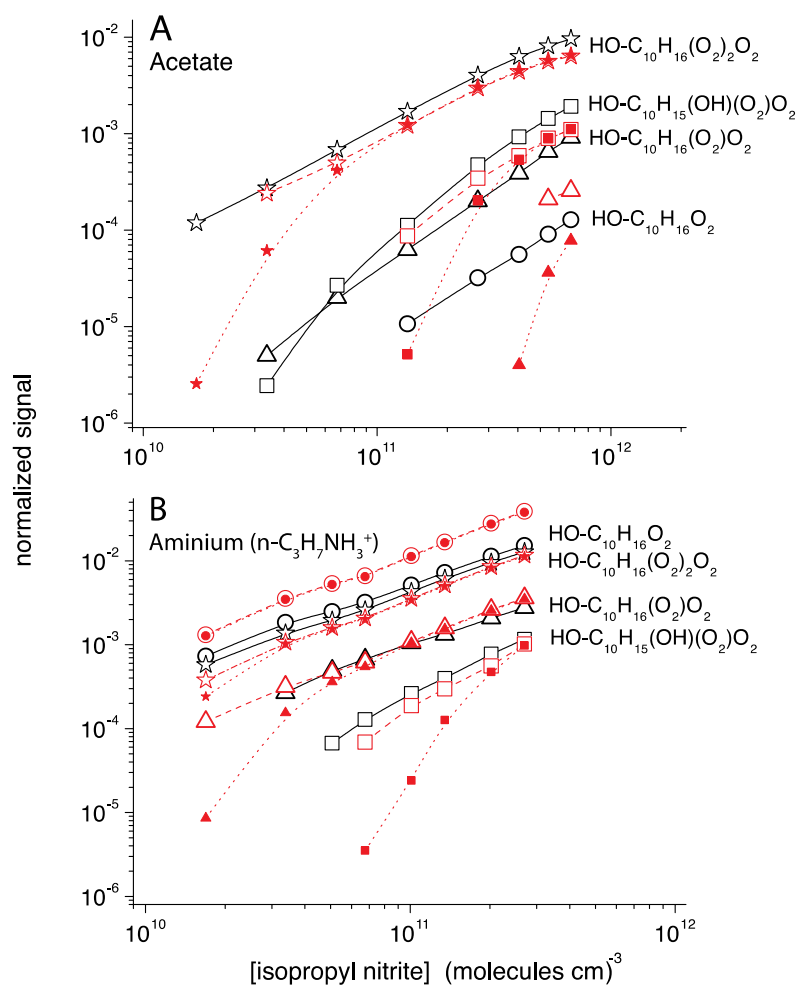


373 **Figure 1.** (A) Linearity of the Orbitrap as a function of normalized signal measured with protonated n-  
 374 propylamine ( $n\text{-C}_3\text{H}_7\text{NH}_3^+$ ) and acetate ( $\text{CH}_3\text{COO}^-$ ) reagent ions with the Orbitrap-Tropos and nitrate-  
 375 ion based chemistry with the Orbitrap-IRCELYON, using identical parameter settings. All signal  
 376 intensities were corrected with respect to the sum of  $(\text{CH}_3\text{COOH})_n\text{-CH}_3\text{COO}^-$  ( $n = 0,1$ ) at nominal 59  
 377 Th and 119 Th; to the sum of  $(n\text{-C}_3\text{H}_7\text{NH}_2)_m\text{-n-C}_3\text{H}_7\text{NH}_3^+$  ( $m = 0,1$ ) at nominal 60 Th and 119 Th; and  
 378 to the sum of  $(\text{HNO}_3)_p\text{-NO}_3^-$  ( $p = 0,1,2$ ) at nominal 62, 125, 188 Th, for the respective reagent ions.  
 379 The black fit is the “sigmoidal correction function” based on a sigmoidal fitting algorithm. (B) Impact  
 380 of the AGC target on the linearity of the CI-Orbitrap-Tropos using aminium ( $n\text{-C}_3\text{H}_7\text{NH}_3^+$ ) as the  
 381 reagent ion.  
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385 **Figure 2.** Mass spectra of ions at nominal  $m/z$  245 from the combined ozonolysis and OH radical386 reaction of  $\alpha$ -pinene for different reaction conditions (A) measured with the CI-Orbitrap and (B)387 comparison of the ion signals recorded by the CI-Orbitrap and the CI-APi-TOF.  $C_9^{13}CH_{16}O_3$ 388 represents most likely the  $^{13}C$ -isotope of pinonaldehyde and  $C_{10}H_{17}O_3$  the initial  $RO_2$  radical from the389 OH attack,  $HO-C_{10}H_{16}O_2$ . Concentrations are given in molecules  $cm^{-3}$ .

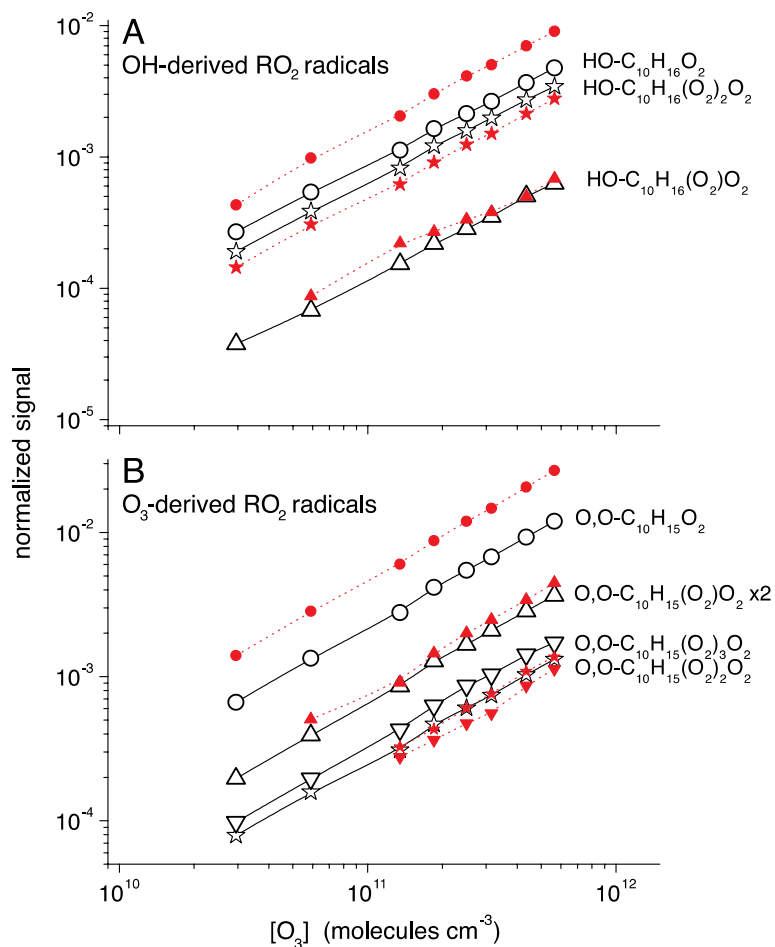


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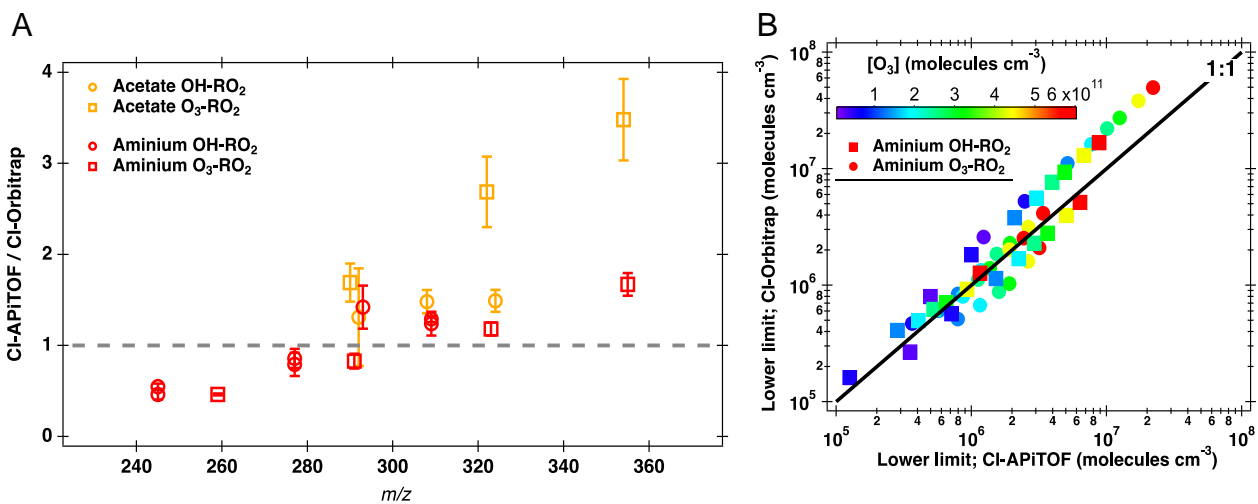
391 **Figure 3.** Normalized signals of RO<sub>2</sub> radicals produced from the OH radical-initiated oxidation of  $\alpha$ -  
 392 pinene as a function of initial IPN concentration measured by the CI-API-TOF (black) and the CI-  
 393 Orbitrap (red). OH radicals have been formed via IPN photolysis. Full and open markers in red  
 394 correspond to raw and corrected (using the sigmoidal correction function) signals measured with the  
 395 Orbitrap, respectively. (A) Acetate and (B) aminium ( $n\text{-C}_3\text{H}_7\text{NH}_3^+$ ) served as the reagent ion for  
 396 otherwise identical reaction conditions in both cases.

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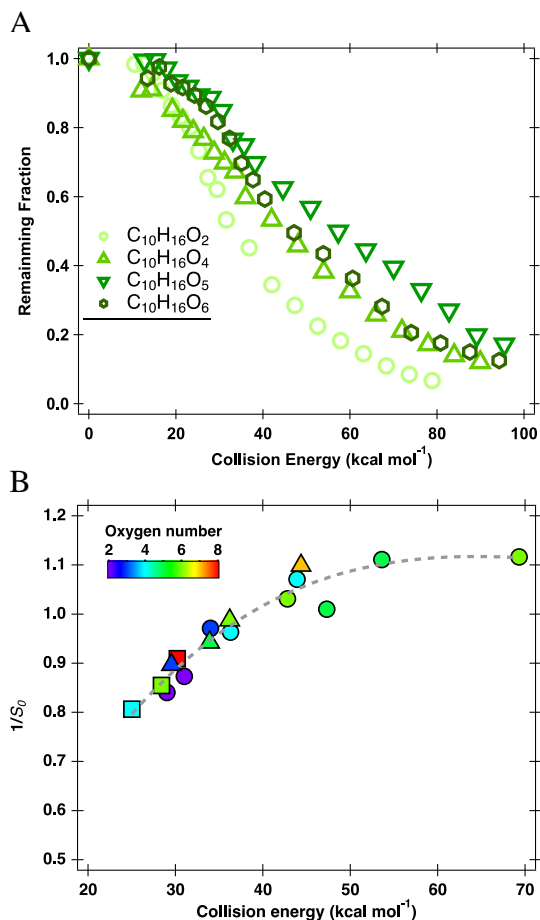


399  
 400 **Figure 4.** Normalized signals of **A)** OH-derived RO<sub>2</sub> radicals and **B)** O<sub>3</sub>-derived RO<sub>2</sub> radicals  
 401 produced from the O<sub>3</sub>/OH + α-pinene reaction as a function of the ozone concentration. Results  
 402 obtained by the CI-API-TOF are given in black and those from the CI-Orbitrap in red using aminium  
 403 (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>) ionization in both cases. The Orbitrap data were corrected using the sigmoidal  
 404 correction function.  
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 407 **Figure 5.** (A) Comparison between lower limit RO<sub>2</sub> radical concentrations measured with the CI-  
 408 APiTOF and the CI-Orbitrap in the different experiments. (B) Correlation of the concentrations of  
 409 RO<sub>2</sub> radicals formed from the O<sub>3</sub>/OH +  $\alpha$ -pinene reaction measured by the CI-API-TOF and the CI-  
 410 Orbitrap using aminium (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>) ionization.

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**Figure 6.** Declustering scans of (A) C<sub>10</sub>H<sub>16</sub>O<sub>2-6</sub> measured from the OH-initiated oxidation of  $\alpha$ -pinene with the CI-Orbitrap using aminium (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>). (B) Relationship between fitting declustering scans (1/S<sub>0</sub>) as a function of collision energy. CE<sub>50</sub> is used as a measured of the relative binding energy and corresponds to the collision energy where half of the signal is removed. S<sub>0</sub> is the maximum amplitude obtained from the sigmoidal fit of declustering scans (e.g., Figure S7) of RO<sub>2</sub> radicals (triangle markers) and OVOCs (ON: square markers; non-ON: circle markers) formed from OH-initiated oxidation of  $\alpha$ -pinene with the CI-Orbitrap using aminium (n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>).

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450

451 SUPPORTING INFORMATION

452 Figure S1 depicts the schematic of a Q Exactive mass spectrometer. Figure S2 shows the mass spectra  
453 of ions at  $m/z$  245 and 260 measured during the oxidation of  $\alpha$ -pinene. Figures S3 and S4 present the  
454 normalized signals of the organic nitrates and carbonyls produced from the OH-initiated oxidation of  
455  $\alpha$ -pinene, respectively. Figure S4 shows the correlation of the concentration measured species using  
456 both instruments and formed from the OH radical initiated oxidation of  $\alpha$ -pinene using acetate-ion-  
457 based ( $\text{CH}_3\text{COO}^-$ ) ionization. Figure S6 presents the normalized signals of  $\text{RO}_2$  generated from the  
458 oxidation of  $\alpha$ -pinene measured using aminium ( $n\text{-C}_3\text{H}_7\text{NH}_3^+$ ). Figure S7 presents the declustering  
459 experiments performed on OVOCs formed from  $\alpha$ -pinene ozonolysis. Figure S8 shows the mass  
460 Spectra of the different perfluorinated acids measured with CI-Orbitrap. Figure S9 presents the relative  
461 ion transmission fit determined using the depletion method. The Supporting Information is available  
462 free of charge on the ACS Publications website.

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