# FA-SIFT study of the reactions of $H_3O^+.(H_2O)_n$ (n=0,1,2), $NO^+$ and $O_2^{\bullet+}$ with the terpenoid aldehydes citral, citronellal and myrtenal and their alcohol analogues

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## Abstract

Biogenic volatile organic compounds (BVOCs) significantly contribute to atmospheric chemistry, air quality and climate. On-line detection of these compounds can be performed by Selected Ion Flow Tube – Mass Spectrometry (SIFT-MS), provided the rate constants and product ion distributions of the underlying ion/molecule reactions are known. These parameters are presented for the reactions of the SIFT-MS reagent ions $H_3O^+.(H_2O)_n$ (n=0-2), $NO^+$ and $O_2^{\bullet+}$ with the terpenoid aldehydes citral, citronellal and myrtenal and the terpenoid alcohols citronellol and myrtenol. The experiments were performed at 295 K and 1.5 hPa in a Flowing Afterglow Selected Ion Flow Tube (FA-SIFT) instrument. All studied reactions proceed at the collision rate which is beneficial for the BVOC detection sensitivity. Non-dissociative proton transfer, and elimination of a water molecule or simultaneous ejection of a water molecule and $C_4H_8$ following protonation were observed as the major mechanisms for most $H_3O^+$ reactions. Reactions of $H_3O^+.(H_2O)$ mainly proceeded by non-dissociative proton transfer, possibly followed by ejection of a water molecule, whereas the main observed mechanism for $H_3O^+.(H_2O)_2$ reactions was ligand switching followed by elimination of up to three water molecules. Charge transfer occurred for all $NO^+$ reactions and was accompanied by other major mechanisms such as hydride transfer and/or elimination of a water molecule following charge transfer and/or ternary association. The $O_2^{\bullet+}$ reactions generally resulted in strong fragmentation. The product ion distributions suggest that selective detection of some

isomeric terpenoids might be possible. However, interference with simultaneously emitted monoterpenes could be a problem.

Keywords: FA-SIFT, SIFT-MS, ion/molecule reactions, terpenoids, aldehydes, alcohols

## 1. Introduction

Terrestrial vegetation is a huge source of non-methane volatile organic compounds (VOCs), also referred to as biogenic VOCs or BVOCs, of which terpene hydrocarbons and their oxygenated derivatives (alcohols, aldehydes, ketones, ethers, acids, ...) constitute an important fraction [1]. Because of their large emission rates and their high reactivity towards the main atmospheric oxidants [2], these compounds play a major role in both gas-phase and particle-phase atmospheric chemistry. They have a strong impact on the oxidative power of the atmosphere by being a sink of $OH^{\bullet}$ radicals (and thus influencing climate by affecting the budget of atmospheric $CH_4$, a major greenhouse gas) and by influencing tropospheric $O_3$ levels. Furthermore, terpene oxidation products contribute to the formation and growth of secondary organic aerosols, SOA, affecting air quality and climate as well [3].

Apart from influencing atmospheric chemistry, BVOC emissions are also believed to play a role in plant functioning, e.g. by attracting pollinators or herbivore predators, deterring herbivores, mediating plant-plant communication and by protecting the plant against excessive heat or oxidative stress [4].

Whereas Gas Chromatography-Mass Spectrometry (GC-MS) can be considered the standard technique to measure BVOCs, recently developed fast and sensitive on-line chemical ionization mass spectrometry techniques, such as Selected Ion Flow Tube-Mass Spectrometry (SIFT-MS) and Proton Transfer Reaction-Mass Spectrometry (PTR-MS), are steadily gaining importance in BVOC research. Those techniques are based on chemical ionization of the BVOCs by reaction with appropriate reactant ions ($H_3O^+$, $NO^+$ and $O_2^{\bullet+}$ in SIFT-MS, mainly $H_3O^+$ in PTR-MS), resulting in specific product ions. Details on the techniques can be found in some excellent recent reviews ([5] for SIFT-MS, [6] for PTR-MS). Rate constants and product ion distributions of the occurring reactant ion/BVOC reactions are required for absolute BVOC quantification. In previous years, several systematic laboratory SIFT-MS and

PTR-MS ion/molecule reaction studies have been carried out in which these reaction parameters were obtained for several terpenoid compounds (hemi-, mono- and sesquiterpenes, terpenoid alcohols and some terpenoid ethers and esters) (reviewed in [7]). However, to the best of our knowledge, no information is available yet on terpenoid aldehydes.

In this paper, calculated absolute rate constants, measured relative rate constants and measured product ion distributions are presented for the reactions of the SIFT reagent ions $H_3O^+$, $NO^+$ and $O_2^{\bullet+}$ with the monoterpenoid aldehydes citronellal and myrtenal, along with their corresponding alcohols citronellol and myrtenol, respectively. Reactions with citral, which is a mixture of neral and geranial, were studied as well. Ion/molecule reaction parameters for the corresponding alcohols nerol and geraniol have been reported previously [8]. When analyzing moist air samples by SIFT-MS, reactant $H_3O^+$ ions efficiently react with $H_2O$ molecules by ternary association to form higher-order proton hydrates. Therefore reactions of the BVOCs with $H_3O^+.(H_2O)_n$ (n=1,2) have also been studied. The chemical structure of the studied BVOCs is shown in Figure 1.

Citral, citronellol and citronellal are important constituents of the essential oils of several plant species [9]. They have been identified as major components in the headspace of fresh leaves of many citrus species [10,11] and are often used indoors as fragrance compounds in air fresheners, cleaning products and as insect repellents. Since the gas-phase reactions of citronellol with $O_3$ and OH [12], of citronellal with $O_3$ and OH [13] and of citral with $O_3$ [14] were all found to be fast, not only the compounds themselves, but also their oxidation products may well contribute to indoor pollution. All three compounds have also been reported to possess antimicrobial effects [15].

Myrtenal was found to be emitted directly by loblolly pine (*Pinus taeda*) branches [16] and the dependence of the myrtenal emission rates on environmental parameters (light intensity, temperature, ...) was integrated in Version 2.1 of the Model for the Emissions of Gases and Aerosols by Nature, MEGAN [17]. Both myrtenal and myrtenol have also recently been identified in SOA from β-pinene ozonolysis [18], whereas myrtenol had been identified previously as a minor gas phase product of β-pinene ozonolysis [19].

## 2. Experimental setup

### 2.1 Instrument

The gas phase ion/molecule reaction studies have been carried out in a Flowing Afterglow-Selected Ion Flow Tube instrument (FA-SIFT) at 295 K and at a pressure of 1.5 hPa. Only a brief description of the instrument will be given here, since it has been amply described in previous papers [20,21]. Reactant ions are produced in a flowing afterglow reactor, transported by an Ar buffer gas flow, sampled into a first vacuum chamber and pre-selected according to their m/z ratio by a first quadrupole mass filter. Ions that are transmitted by the filter are subsequently injected in the He buffer gas flow of the SIFT reactor by means of a Venturi injector. At a fixed distance downstream of the reactant ion injection point, controlled flows of the pure BVOC diluted in He are added to the main He buffer gas flow, resulting in product ion formation. At the downstream end of the reactor, a small fraction of the ions is sampled into a second vacuum chamber, analyzed according to their m/z ratio and subsequently detected by a secondary electron multiplier with conversion dynode.

In previous ion/molecule reaction studies with this apparatus, product ion distributions have been obtained by introducing the neutral reactant close to the mass spectrometer sampling orifice in order to avoid corrections for the mass-dependent differential diffusion of the ions to the reactor walls. In this study the terpenoid compounds were introduced via a ring-shaped inlet which is also used for kinetic measurements and is located 27.8 cm upstream the sampling point, corresponding with an experimentally determined reaction time of 2.8 ± 0.3 ms. Consequently much smaller BVOC concentrations are required in the SIFT reactor to obtain the same decrease of the reactant ion signal due to reaction than when BVOCs are introduced through the inlet near the sampling orifice. This firmly reduces the risk for condensation of the low vapor pressure terpenoid aldehydes and alcohols in the pumps of the instrument. The BVOC flow was dynamically diluted prior to entering the reactor by sending a small He flow (20 sccm = 0.034 Pa $m^3$ $s^{-1}$) over the surface of the pure liquid BVOC sample stored in a glass vial, which was completely immersed in a thermostatted bath. Controlling the BVOC flow was then accomplished by changing the pressure above the liquid through variation of the conductance of a heated needle valve (333 K) between the liquid reservoir and the SIFT reactor.

## 2.2 Methodology

### 2.2.1 Rate constants

Absolute ion/BVOC rate constant measurements with the SIFT apparatus require the introduction of controlled and well-quantified BVOC flows in the reactor. In previous studies (e.g. [22]), this was often accomplished by monitoring the pressure decrease in a volume-calibrated glass bottle containing a dilute mixture of the BVOC in He with known mixing ratio. The BVOC flow into the reactor was controlled by adjusting a heated needle valve between the glass bottle and the reactor. However, for the compounds under study here, attempts to produce stable static BVOC mixtures failed because of the stickiness of these compounds.

A second method for introducing controlled and quantified BVOCs uses the same set-up as described in paragraph 2.1. However, in order to quantify the BVOC flow with this method, accurate values of the BVOC vapor pressure at the temperature of the glass reservoir are required and this information is not available for the studied compounds.

Therefore absolute rate constant measurements could not be performed and we had to rely on theoretical calculations of the $H_3O^+$/BVOC collision rate constants to determine the reaction rate constants of the other reactant ion species ($H_3O^+.H_2O$, $H_3O^+.(H_2O)_2$, $NO^+$, $NO^+.H_2O$ and $O_2^{\bullet+}$) with the BVOCs in a relative way. This is a sound way to do since many experimental studies have shown that exothermic $H_3O^+$/molecule reactions invariably proceed at the collision rate [23].

#### 2.2.1.1 Rate constant calculations

Absolute $H_3O^+$/BVOC collision rate constants were calculated using the parameterized equation of Su and Chesnavich [24,25], using values for the polarizability ($\alpha$) and the electric dipole moment ($\mu_D$) of the BVOCs obtained from quantum chemical calculations (because of lack of experimental data). As the required computed molecular parameters depend strongly on the conformation, first a conformational analysis was performed for all molecules. Such a detailed conformational analysis was carried out by combining a MMFF [26,27] random search with a MM3/MM4 [28,29] stochastic search [30]. The minima that were found were optimized at the B3LYP/6-31G(d,p) level and the Hessian was calculated to ensure that all

located stationary points were minima. All minima within an energy window of 16.75 kJ mole$^{-1}$ were then re-optimized with the aug-cc-pVDZ basis set, and $\alpha$ and $\mu_D$ were calculated for each minimum. All calculations were performed in the Ghent University scientific computing environment using Gaussian09 [31]. Collision rate constants were calculated for all individual conformations of a compound and subsequently Boltzmann-averaged using the enthalpy to obtain a conformational population. The enthalpy was calculated at 295.15 K and 1.5 hPa via DFT using standard expressions [32]. Vibrational frequencies were scaled by a factor 0.970 [33].

Calculations of $H_3O^+$/VOC collision rate constants performed in previous studies using the above-described methodology [8,34] resulted in a good agreement with experimental rate constant values obtained with our SIFT instrument.

2.2.1.2 Relative rate constant measurements

The $O_2^{\bullet+}$/BVOC rate constants were obtained relative to the $H_3O^+$/BVOC rate constants by simultaneously producing stable currents of both ion species in the flowing afterglow (FA) reactor. This was accomplished by adding a small amount of water vapor to the Ar buffer gas flow via a first reactant gas inlet in order to partially convert $Ar^+$ ions, produced by electron ionization using an emission current-controlled Thoria-coated Iridium filament, into a current of $H_3O^+$ ions and by adding a small flow of laboratory air via a second reactant gas inlet to convert the remaining $Ar^+$ ions to $O_2^{\bullet+}$ by reaction with $O_2$. The $O_2^{\bullet+}$ and $H_3O^+$ ions were sequentially transmitted by the selection quadrupole mass filter and introduced in the SIFT reactor in the absence ($I(O_2^{\bullet+})_0$ and $I(H_3O^+)_0$) and in the presence of BVOC in the SIFT reactor at different concentrations [M] ($I(O_2^{\bullet+})_M$ and $I(H_3O^+)_M$). The rate constant ratio $k(O_2^{\bullet+})/k(H_3O^+)$ was obtained as the slope of the linear fit of $\ln(I(O_2^{\bullet+})_M/ I(O_2^{\bullet+})_0)$ versus $\ln(I(H_3O^+)_M/ I(H_3O^+)_0)$.

In a similar way, $O_2^{\bullet+}$ and $NO^+$ reactant ions were produced simultaneously in the flowing afterglow reactor by simultaneous addition of small air and NO flows, allowing to infer the rate constant ratio $k(NO^+)/k(O_2^{\bullet+})$.

The rate constant ratios $k(H_3O^+.H_2O)/k(H_3O^+)$ and $k(H_3O^+.(H_2O)_2)/k(H_3O^+.H_2O)$ were obtained by adding appropriate amounts of water vapor to the FA reactor and pre-selecting $H_3O^+.H_2O$ and $H_3O^+.(H_2O)_3$ ions, respectively. Partial break-up of $H_3O^+.H_2O$ to $H_3O^+$ upstream the reaction zone was accomplished by increasing the electric field in the vicinity of

the SIFT injection orifice. The ratio $k(H_3O^+.H_2O)/k(H_3O^+)$ was obtained as the slope of $\ln(I(H_3O^+.H_2O)_M/ I(H_3O^+.H_2O)_0)$ versus $\ln(I(H_3O^+)_M/ I(H_3O^+)_0)$.

In order to produce a stable and sufficiently intense $H_3O^+.(H_2O)_2$ current (resulting in > 1000 cps) in the SIFT reactor, $H_3O^+.(H_2O)_3$ ions were pre-selected and subjected to collision-induced dissociation at the SIFT injector. By further increasing the electric field near the orifice, break-up of $H_3O^+.(H_2O)_3$ ions led to the simultaneous and stable production of both $H_3O^+.(H_2O)_2$ and $H_3O^+.H_2O$ ion currents in the SIFT reactor. The ratio $k(H_3O^+.(H_2O)_2)/k(H_3O^+.H_2O)$ was then obtained as the slope of $\ln(I(H_3O^+.(H_2O)_2)_M/ I(H_3O^+.(H_2O)_2)_0)$ versus $\ln(I(H_3O^+.H_2O)_M/ I(H_3O^+.H_2O)_0)$.

The experimentally obtained rate constant ratios were then combined with the calculated $H_3O^+$/BVOC collision rate constant to obtain absolute rate constant values for the BVOC reactions with the other reactant ions.

The rate constant ratio $k(NO^+.H_2O)/k(NO^+)$ was obtained by injecting $NO^+$ ions into the SIFT, adding controlled water vapor flows to the SIFT reactor and monitoring the $NO^+$ and $NO^+.H_2O$ ion signals at different water vapor concentrations [35].

### 2.2.2 Product ion distributions

Product ions were identified by taking full mass spectra after which their ion signals were recorded in the multiple ion monitoring mode, using at least three different BVOC concentrations in the SIFT reactor. The product ion signals were subsequently corrected for background contributions, mass discrimination and diffusion enhancement. Mass discrimination of the instrument was obtained by sequentially injecting high purity currents of single ion species $X^+$ into the SIFT and by simultaneously recording the corresponding current (I) on the mass spectrometer inlet plate and the ion count rate (S) obtained with the mass spectrometer. The $X^+$ species used for this purpose were, in addition to $H_3O^+$, $H_3O^+.H_2O$ and $SF_5^+$, primary and secondary product ions of proton hydrates with 1-penten-3-ol, isopropanol and ethanol and encompassed m/z values between 19 and 155. The mass discrimination factor (MDF) for these ion species was determined as the ratio $S/I(H_3O^+)$ to $S/I(X^+)$. MDF values for the specific product ions of the studied ion/molecule reactions were obtained from a polynomial fit through $S/I(X^+)$ versus $m/z(X^+)$. MDF-corrected product ion signals were obtained by multiplying the background corrected ion signals by their corresponding MDF value.

As already mentioned, diluted BVOC mixtures were introduced upstream of the mass spectrometer inlet and consequently differential diffusion of the precursor ($S^+$) and product ($P^+$) ions in the helium buffer gas had to be accounted for in order to obtain correct product ion distributions. This was accomplished by dividing the MDF-corrected product ion count rates by their respective diffusion enhancement factor, which is given by [36]:

$$DE(P^+) = \frac{e^{\frac{D_p(S^+)-D_p(P^+)}{\Lambda^2}\tau} - 1}{e^{\frac{D_p(S^+)-D_p(P^+)}{\Lambda^2}\tau}}$$

In this formula, which is only valid for small concentrations of the reactant BVOC, $\Lambda$ and $\tau$ are the characteristic length of the reactor and the reaction time, respectively. The former is obtained by the formula [37]:

$$\frac{1}{\Lambda^2} = \left(\frac{2.405}{r_0}\right)^2 + \left(\frac{\pi}{H}\right)^2$$

with $r_0$ and H the radius of the reactor (2.0 cm) and the length of the reactor zone (27.8 cm), respectively, resulting in a value for $\Lambda$ of 0.828 cm for our specific configuration.

The reaction time $\tau$ was determined experimentally by putting a short voltage pulse on the electrically insulated BVOC inlet and by measuring the arrival of the ion current perturbation on the mass spectrometer detector, the ion flight time in the mass spectrometer being negligible compared to the ion residence time between the BVOC inlet and the mass spectrometer inlet. This reaction time was found to be 2.8 ± 0.3 ms.

The free diffusion coefficient $D_p$ of a specific ion species is related to its ion mobility K by the Nernst-Townsend-Einstein equation:

$$D_p = K\frac{k_b T}{q}$$

with $k_b$, q and T the Boltzmann constant, the electrical charge of the ion and the temperature of the reactor, respectively. The ion mobility itself is calculated from standard ion mobility values taking into account the actual pressure and temperature in the reactor. Standard ion

mobility values for the different precursor and product ions in this work were obtained from a fit through calculated $K_0$ values, reported by Dryahina et al. [38], versus m/z. For this fit only the proton hydrates and organic ions mentioned in Table 1 of [38] were withheld.

### 2.3 Chemicals

All studied BVOCs were obtained from Sigma-Aldrich. The optically active compounds (1R)-Myrtenal, (1R)-(-)-myrtenol, (R)-(+)-citronellal and (R)-(+)-beta-citronellol had a stated purity of 98, 95, 98 and 98%, respectively. Citral is a racemic mixture of neral and geranial and had a purity of 95%. The buffer gases He and Ar were obtained from Air Products and both were 99.9997% pure.

## 3. Results and discussion

### 3.1 Rate constants

The calculated ion/BVOC collision rate constants are shown in Table 1, along with the quantum chemically obtained electrical dipole moments and polarizabilities. Also shown are the absolute reaction rate constants of $H_3O^+.H_2O$, $H_3O^+.(H_2O)_2$, $NO^+$, $NO^+.H_2O$ and $O_2^{\bullet+}$ with the studied BVOCs, obtained by using the calculated $H_3O^+$/BVOC collision rate constants and experimentally determined rate constant ratios $k(O_2^{\bullet+})/k(H_3O^+)$, $k(H_3O^+.H_2O)/k(H_3O^+)$, $k(H_3O^+.(H_2O)_2)/k(H_3O^+.H_2O)$, $k(NO^+)/k(O_2^{\bullet+})$ and $k(NO^+.H_2O)/k(NO^+)$. The precision of the first four rate constant ratios is 1%, resulting in a precision of less than 2% for the resulting absolute rate constant. A precision of 3% was obtained for the latter rate constant ratio, which was determined in a different way (see paragraph 2.2.1.2).

The calculated and experimentally obtained rate constants all show a good agreement, indicating that all studied ion/molecule reactions proceed at the collision limit, which is beneficial to the BVOC detection sensitivity by SIFT-MS.

### 3.2 Product ion distributions

The product ion distributions of $H_3O^+.(H_2O)_n$ (n=0,1,2), $NO^+$ and $O_2^{+\bullet}$ with citral, citronellal, myrtenal, citronellol and myrtenol are gathered in Table 2. Only product ion species with branching ratios higher than the impurity of the compound have been tabulated and isotopic

abundances were taken into account when calculating branching ratios. Tentative identification of the product ions is based on whether they form hydrates upon addition of water vapor to the SIFT reactor, as oxygenated hydrocarbon ions have a propensity to form hydrates, whereas pure hydrocarbon ions do not [39]. The relative error on individual branching ratios was found to be better than 3% for branching ratios above 80%, between 3 and 7% for branching ratios between 50 and 80%, between 7 and 12% for branching ratios between 30 and 50% and varied between 6 and 24% for branching ratios between 2 and 30%.

3.2.1 Reactions with $H_3O^+.(H_2O)_n$ (n=0,1,2)

All studied $H_3O^+$/M reactions were found to proceed by exothermic proton transfer, resulting in the nascent excited protonated molecule $(MH^+)^*$, which is either stabilized by collisions with a third body (He) or releases its excess energy by fragmentation. This is exemplified in the reaction of $H_3O^+$ with myrtenol (R1) for which the three major pathways are non-dissociative proton transfer (R1a), elimination of a water molecule following protonation (R1b), and ejection of $C_4H_{10}O$ following protonation (R1c). The latter pathway most probably involves simultaneous ejection of $H_2O$ and $C_4H_8$.

$$H_3O^+ + C_{10}H_{16}O \rightarrow (C_{10}H_{17}O^+)^* + H_2O \quad (R1)$$

$$(C_{10}H_{17}O^+)^* + He \rightarrow C_{10}H_{17}O^+ + He \quad (R1a)$$

$$(C_{10}H_{17}O^+)^* \rightarrow C_{10}H_{15}^+ + H_2O \quad (R1b)$$

$$\rightarrow C_6H_7^+ + [H_2O + C_4H_8] \quad (R1c)$$

$$\rightarrow C_4H_9^+ + C_6H_8O \quad (R1d)$$

$$\rightarrow C_7H_9^+ + C_3H_8O \quad (R1e)$$

$$\rightarrow C_{10}H_{15}O^+ + H_2 \quad (R1f)$$

Several SIFT studies have shown that water elimination after protonation is a common mechanism for saturated and unsaturated, non-phenolic alcohols [8,34,39,40], strongly limiting the contribution of the non-dissociative proton transfer channel. The $H_3O^+$/myrtenol reaction follows this general observation, but this is not really the case for the $H_3O^+$/citronellol reaction which has an $MH^+$ contribution of 49%.

Water elimination following protonation is also an important process for citral and citronellal, but is completely absent for myrtenal. This observation confirms the hypothesis, put forward in previous systematic SIFT-MS studies on both saturated and unsaturated aldehydes [41,42], that this process is restricted to those aldehydes which can form a cyclic six-membered intermediate structure upon protonation (containing 4 Cs, O and H), which is clearly impossible for the nascent excited protonated myrtenal molecule.

Several SIFT-MS and PTR-MS studies reported that the major product ions of $H_3O^+$/monoterpene ($C_{10}H_{16}$) reactions are the stabilized proton transfer product $C_{10}H_{17}^+$ (m/z 137) and a typical fragment $C_6H_9^+$ (m/z 81) due to ejection of $C_4H_8$ [22,43,44]. The same difference in mass between the two major fragment ions is now encountered in the reactions of three monoterpenoids (myrtenol (152 u), citronellol (156 u) and citronellal (154 u)) and also in a previous study of the reactions of $H_3O^+$ with linalool (154 u), nerol (154 u) and geraniol (154 u) [8], irrespective of the mass of the protonated terpenoid. This indicates that the simultaneous occurrence of ions at m/z values x, x-18 and x-74 in mass spectra may point to the presence of monoterpenoid alcohols and aldehydes of molecular mass x-1, but it is not a general rule. Indeed, ejection of a $C_4H_8$ molecule from the major fragment (at m/z 135) clearly does not take place in the case of the citral molecule for which major fragments at m/z 95 ($C_7H_{11}^+$) and at m/z 59 ($C_3H_7O^+$) have been observed.

Next to the three above-mentioned reaction channels, the $H_3O^+$/myrtenol reaction also results in the formation of fragment ions at m/z 57 ($C_4H_9^+$) and 93 ($C_7H_9^+$), and in ejection of a hydrogen molecule following protonation. The latter process was also observed as a minor channel in the reactions of $H_3O^+$ with the terpenoid alcohols verbenol [40] and geraniol [8]. The $H_3O^+$/citronellol and $H_3O^+$/citronellal reactions also led to a product ion at m/z 57 ($C_4H_9^+$) and 95 ($C_7H_{11}^+$), respectively. Small contributions (2-3%) of product ions at m/z 95 have also been reported for the acyclic terpenoid alcohols linalool, nerol and geraniol ($C_{10}H_{18}O$, 154 u) [8], which are all isomers of citronellal.

The reactions of $H_3O^+.H_2O$ with the studied compounds mainly proceed by non-dissociative proton transfer (and even exclusively in the case of citronellol and myrtenal) and water elimination following proton transfer, as exemplified by the reaction with citronellal (R2).

$$H_3O^+.H_2O + C_{10}H_{18}O \rightarrow C_{10}H_{19}O^+ + 2H_2O \qquad \text{(R2a)}$$

$\rightarrow C_{10}H_{17}^{+} + 3H_2O$ (R2b)

The lower exothermicity with respect to $H_3O^+$ reactions is sufficient to avoid additional ejection of $C_4H_8$. The $H_3O^+.H_2O$/citral reaction, however, still results in product ions at m/z 95, but the channel leading to m/z 59 ions is no longer energetically accessible.

The reactions of $H_3O^+.(H_2O)_2$ proceed by ligand switching followed by elimination of up to 3 water molecules and is exemplified by the $H_3O^+.(H_2O)_2$/citronellal reaction (R3).

$$H_3O^+.(H_2O)_2 + C_{10}H_{18}O \rightarrow C_{10}H_{21}O_2^{+} + 2H_2O \quad \text{(R3a)}$$
$$\rightarrow C_{10}H_{19}O^{+} + 3H_2O \quad \text{(R3b)}$$
$$\rightarrow C_{10}H_{17}^{+} + 4H_2O \quad \text{(R3b)}$$

Apart from the product ions that are mentioned in Table 2 and which have a contribution larger than the impurity of the substance (5%), the $H_3O^+.(H_2O)_2$/citral reaction also results in product ions at m/z 95 ($C_7H_{11}^{+}$) and 135 ($C_{10}H_{15}^{+}$), with contributions of 4 and 3%, respectively.

3.2.2 Reactions with $NO^+$

Charge transfer is the major reaction path for all $NO^+$ reactions indicating that the ionization energy for all studied compounds must be lower than the one of NO, which is 9.26 eV. This mechanism is especially dominant for citronellol, citronellal and myrtenol (79, 68 and 69%, respectively). Elimination of a water molecule following charge transfer is only observed for citronellal and citronellol. Similar to the $H_3O^+$/myrtenal reaction, ejection of a water molecule from the nascent excited myrtenal$^{+*}$ ion does not take place because a six-membered ring structure, required for a McLafferty rearrangement [45], cannot form.

Myrtenal is also the only compound for which an association channel was observed. This suggests that the difference in ionization energies of NO and myrtenal is probably sufficiently small to allow charge delocalization around the (NO.myrtenal)$^{+*}$ intermediate ion, hereby increasing its lifetime and allowing collisional stabilization [42].

Hydride ($H^-$) transfer, the second major pathway for myrtenal and citral, is a well-known mechanism for reactions of $NO^+$ with both alcohols [8,34,39,40] and aldehydes [41,46] and results in HNO formation. This pathway is less important for citronellal (only 7%) and really minor for the studied alcohols. Hydroxide transfer leading to $HNO_2$ formation, another frequently observed mechanism for $NO^+$/alcohol reactions in SIFT-MS conditions, does not occur for any of the compounds in the present study.

Specific fragmentations (with contributions larger than 3%) were observed for myrtenol (production of $C_8H_{12}^+$ ions at m/z 108) and for citral (production of $C_3H_7O^+$ and $C_7H_{10}^+$ ions at m/z 59 and 94, respectively).

### 3.2.3 Reactions with $O_2^+$

Reactions of $O_2^+$ with many BVOCs proceed via dissociative charge transfer and are generally highly exothermic because of the high ionization energy of $O_2$ (12.07 eV). This results in strong fragmentation of the nascent excited charge transfer product and consequently in a large number of product ion species. This was also the case in the present study. Whereas the contribution of the non-dissociative charge transfer channel varied between 15 and 20% for the terpenoid aldehydes, it was found to be only 2% for the alcohols (therefore not shown in Table 2). Other easily identifiable reaction mechanisms that took place were elimination of a water molecule or of a methyl radical following charge transfer. Most major fragment ions were also present in the electron ionization spectra of the molecules [47].

### 3.2.4 Feasibility of isomer distinction

Several isomeric terpenoid alcohols and aldehydes, among others citronellal, geraniol, nerol and linalool are co-emitted by fresh leaves of citrus species and their abundances are generally strongly variety-dependent [10,11]. The present data, in combination with previously reported data on the three alcohols [8], indicate an important difference in the contribution of the collisionally stabilized protonated molecules to the corresponding product ion distributions of their reaction with $H_3O^+$. Whereas this contribution is 25% for citronellal, it is only 4% for linalool and below 4% for nerol and geraniol. A rather similar difference was found for the stabilized charge transfer product in the $O_2^{\bullet+}$ product ion distributions.

The feasibility of performing unambiguous concentration measurements of citronellal based on the product ion signal at m/z 155 (protonated citronellal) using $H_3O^+$ reagent ions or at m/z 154 (ionized citronellal) using $O_2^{\bullet+}$ reagent ions, however, will strongly depend on individual mixing ratios of the different isomeric compounds. This will be even more the case when using $NO^+$ reagent ions because of the very similar product ion distributions of the reactions of citronellal, nerol and geraniol with $NO^+$.

Moreover, it should be noted that, when measuring emissions from vegetation, these BVOCs with a molar mass of 154 g/mol can be co-emitted with monoterpenes ($C_{10}H_{16}$). This may result in important interferences for the detection of those terpenoid alcohols and aldehydes as they have major product ions (at m/z 137 and 81) in common with the monoterpenes.

## 4. Conclusion

The rate constants and product ion distributions of the reactions of $H_3O^+.(H_2O)_n$ (n=0,1,2), $NO^+$ and $O_2^{+\bullet}$ with citral, citronellal, myrtenal, citronellol and myrtenol have been determined in support of the detection of these biogenic terpenoid aldehydes and alcohols with SIFT-MS. All reactions were found to occur at the collision limit, which favors detection sensitivity provided that the contribution of the fingerprint product ions to the product ion distributions of the specific BVOCs is sufficiently large.

The measurements show that both $H_3O^+$ and $NO^+$ reagent ions generally seem to be equally well suited for quantification of the studied compounds. In Table 3, the contribution to the product ion distribution of those product ions which can easily be related to the molecular mass of the compound of interest is shown, i.e. those due to non-dissociative proton transfer, water elimination following protonation and additional elimination of $C_4H_8$ in the case of $H_3O^+$ reagent ions. The sum of those product ions makes up between 76 and 96% of all product ions, except for citral for which this contribution is only 51%. Product ions resulting from non-dissociative charge transfer, hydride transfer, water elimination following charge transfer and termolecular association together constitute between 59 and 94% of the product ions for the investigated BVOCs when using $NO^+$ reagent ions. Previously obtained SIFT-MS data on terpenoid alcohols have also been gathered in Table 3, showing that the sum of the product ions corresponding to the specified reaction channels for $H_3O^+$ and $NO^+$ constitutes a major part of all product ions for these species as well. Moreover, the data in Table 3 reveal

once more that the simplistic notion often mentioned in the literature that the main product ion for $H_3O^+$ reactions is the protonated molecule is an exception rather than the rule.

The product ion distributions of the isomeric compounds citronellal, nerol and geraniol indicate that selective detection of citronellal using $H_3O^+$ or $O_2^{\bullet+}$ might be feasible, depending on the differences in abundance of the different compounds in a mixture. However, care should be taken when measuring terpenoid alcohols and aldehydes in the presence of monoterpenes.

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Figure captions

Figure 1: structures of studied terpenoid aldehydes and alcohols

| compound | $\mu_D$ (Debye) | $\alpha$(Å$^3$) | $k_{exp}$ [$k_c$] ($10^{-9}$ cm$^3$s$^{-1}$ molecule$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $H_3O^+$ | $H_3O^+.H_2O$ | $H_3O^+.(H_2O)_2$ | $NO^+$ | $NO^+.H_2O$ | $O_2^{\bullet+}$ |
| citral | 4.39 | 20.3 | [5.9] | 4.5 [4.4] | 3.8 [3.8] | 5.1 [4.8] | | 4.9 [4.7] |
| citronellal | 2.88 | 19.6 | [4.3] | 3.3 [3.2] | 2.9 [2.8] | 3.6 [3.5] | 3.2 [2.9] | 3.5 [3.4] |
| citronellol | 1.62 | 16.6 | [3.1] | 2.2 [2.3] | 1.8 [2.0] | 2.5 [2.5] | 2.3 [2.1] | 2.5 [2.4] |
| myrtenal | 3.91 | 17.8 | [5.3] | 3.8 [4.0] | 3.2 [3.4] | 4.4 [4.3] | 4.0 [3.6] | 4.3 [4.2] |
| myrtenol | 1.71 | 15.1 | [3.0] | 2.3 [2.3] | 1.9 [2.0] | 2.5 [2.5] | 2.4 [2.1] | 2.5 [2.4] |

Table 1: Experimentally determined reaction rate constants ($k_{exp}$) and calculated collision rate constants ($k_c$) for the studied ion/molecule reactions. Dipole moments $\mu_D$ and polarizabilities $\alpha$ are obtained from quantum chemical calculations.

| Molecule formula mass (u) | $H_3O^+$ | | | $H_3O^+.H_2O$ | | | $H_3O^+.(H_2O)_2$ | | | $NO^+$ | | | $O_2^{\bullet+}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | m/z | formula | % | m/z | formula | % | m/z | formula | % | m/z | formula | % | m/z | formula | % |
| citral | 59 | $C_3H_7O^+$ | 11 | 95 | $C_7H_{11}^+$ | 38 | 153 | $C_{10}H_{17}O^+$ | 22 | 59 | $C_3H_7O^+$ | 8 | 59 | $C_3H_7O^+$ | 8 |
| $C_{10}H_{16}O$ | 95 | $C_7H_{11}^+$ | 27 | 135 | $C_{10}H_{15}^+$ | 12 | 171 | $C_{10}H_{19}O_2^+$ | 70 | 94 | $C_7H_{10}^{\bullet+}$ | 20 | 69 | $C_5H_9^+$ | 13 |
| 152 | 135 | $C_{10}H_{15}^+$ | 10 | 153 | $C_{10}H_{17}O^+$ | 49 | others | | 8 | 151 | $C_{10}H_{15}O^+$ | 28 | 84 | $C_5H_8O^{\bullet+}$ | 8 |
| | 153 | $C_{10}H_{17}O^+$ | 41 | Others | | 1 | | | | 152 | $C_{10}H_{16}O^{\bullet+}$ | 31 | 94 | $C_7H_{10}^{\bullet+}$ | 15 |
| | others | | 11 | | | | | | | others | | 13 | 109 | $C_8H_{13}^+$ | 7 |
| | | | | | | | | | | | | | 152 | $C_{10}H_{16}O^{\bullet+}$ | 15 |
| | | | | | | | | | | | | | others | | 34 |
| citronellal | 81 | $C_6H_9^+$ | 23 | 137 | $C_{10}H_{17}^+$ | 35 | 137 | $C_{10}H_{17}^+$ | 7 | 111 | $C_7H_{11}O^+$ | 3 | 84 | $C_5H_8O^{\bullet+}$ | 5 |
| $C_{10}H_{18}O$ | 95 | $C_7H_{11}^+$ | 4 | 155 | $C_{10}H_{19}O^+$ | 64 | 155 | $C_{10}H_{19}O^+$ | 29 | 112 | $C_7H_{12}O^{\bullet+}$ | 3 | 98 | $C_6H_{10}O^{\bullet+}$ | 4 |
| 154 | 137 | $C_{10}H_{17}^+$ | 44 | others | | 1 | 173 | $C_{10}H_{21}O_2^+$ | 64 | 136 | $C_{10}H_{16}^{\bullet+}$ | 13 | 109 | $C_8H_{13}^+$ | 3 |
| | 155 | $C_{10}H_{19}O^+$ | 25 | | | | | | | 153 | $C_{10}H_{17}O^+$ | 7 | 110 | $C_8H_{14}^{\bullet+}$ | 13 |
| | others | | 4 | | | | | | | 154 | $C_{10}H_{18}O^{\bullet+}$ | 68 | 111 | $C_7H_{11}O^+$ | 8 |
| | | | | | | | | | | others | | 6 | 112 | $C_7H_{12}O^{\bullet+}$ | 5 |
| | | | | | | | | | | | | | 121 | $C_9H_{13}^+$ | 7 |
| | | | | | | | | | | | | | 136 | $C_{10}H_{16}^{\bullet+}$ | 10 |
| | | | | | | | | | | | | | 139 | $C_9H_{15}O^+$ | 4 |
| | | | | | | | | | | | | | 154 | $C_{10}H_{18}O^{\bullet+}$ | 20 |
| | | | | | | | | | | | | | others | | 21 |
| citronellol | 57 | $C_4H_9^+$ | 8 | 157 | $C_{10}H_{21}O^+$ | 100 | 157 | $C_{10}H_{21}O^+$ | 70 | 137 | $C_{10}H_{17}^+$ | 3 | 68 | $C_5H_8^{\bullet+}$ | 3 |
| $C_{10}H_{20}O$ | 83 | $C_6H_{11}^+$ | 16 | | | | 175 | $C_{10}H_{23}O_2^+$ | 30 | 138 | $C_{10}H_{18}^{\bullet+}$ | 12 | 69 | $C_5H_9^+$ | 3 |
| 156 | 139 | $C_{10}H_{19}^+$ | 17 | | | | | | | 155 | $C_{10}H_{19}O^+$ | 3 | 71 | $C_4H_7O^+$ | 8 |
| | 157 | $C_{10}H_{21}O^+$ | 49 | | | | | | | 156 | $C_{10}H_{20}O^{\bullet+}$ | 79 | 81 | $C_6H_9^+$ | 12 |
| | others | | 10 | | | | | | | others | | 3 | 82 | $C_6H_{10}^{\bullet+}$ | 16 |
| | | | | | | | | | | | | | 95 | $C_7H_{11}^+$ | 9 |
| | | | | | | | | | | | | | 96 | $C_7H_{12}^{\bullet+}$ | 3 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | 109 | $C_8H_{13}^+$ | 5 |
| | | | | | | | | | | | | | 110 | $C_8H_{14}^{\bullet+}$ | 3 |
| | | | | | | | | | | | | | 123 | $C_9H_{15}^+$ | 12 |
| | | | | | | | | | | | | | 138 | $C_{10}H_{18}^{\bullet+}$ | 7 |
| | | | | | | | | | | | | | others | | 19 |
| myrtenal | 151 | $C_{10}H_{15}O^+$ | 96 | 151 | $C_{10}H_{15}O^+$ | 99 | 151 | $C_{10}H_{15}O^+$ | 23 | 107 | $C_7H_7O^+$ | 3 | 79 | $C_6H_7^+$ | 11 |
| $C_{10}H_{14}O$ | others | | 4 | others | | 1 | 169 | $C_{10}H_{17}O_2^+$ | 75 | 149 | $C_{10}H_{13}O^+$ | 28 | 106 | $C_8H_{10}^{\bullet+}$ | 23 |
| 150 | | | | | | | others | | 2 | 150 | $C_{10}H_{14}O^{\bullet+}$ | 35 | 107 | $C_7H_7O^+$ | 18 |
| | | | | | | | | | | 180 | $C_{10}H_{14}NO_2^+$ | 18 | 108 | $C_7H_8O^{\bullet+}$ | 15 |
| | | | | | | | | | | others | | 16 | 135 | $C_9H_{11}O^+$ | 2 |
| | | | | | | | | | | | | | 150 | $C_{10}H_{14}O^{\bullet+}$ | 17 |
| | | | | | | | | | | | | | Others | | 14 |
| myrtenol | 57 | $C_4H_9^+$ | 5 | 135 | $C_{10}H_{15}^+$ | 78 | 135 | $C_{10}H_{15}^+$ | 85 | 108 | $C_8H_{12}^{\bullet+}$ | 17 | 79 | $C_6H_7^+$ | 35 |
| $C_{10}H_{16}O$ | 79 | $C_6H_7^+$ | 16 | 151 | $C_{10}H_{15}O^+$ | 5 | 189 | $C_{10}H_{21}O_3^+$ | 7 | 152 | $C_{10}H_{16}O^{\bullet+}$ | 69 | 91 | $C_7H_7^+$ | 8 |
| 152 | 93 | $C_7H_9^+$ | 5 | 153 | $C_{10}H_{17}O^+$ | 5 | others | | 8 | others | | 14 | 108 | $C_8H_{12}^{\bullet+}$ | 17 |
| | 135 | $C_{10}H_{15}^+$ | 53 | others | | 12 | | | | | | | 121 | $C_9H_{13}^+$ | 7 |
| | 151 | $C_{10}H_{15}O^+$ | 5 | | | | | | | | | | others | | 33 |
| | 153 | $C_{10}H_{17}O^+$ | 7 | | | | | | | | | | | | |
| | others | | 9 | | | | | | | | | | | | |

Table 2: Product ion distributions of the reactions of $H_3O^+$, $H_3O^+.H_2O$, $H_3O^+.(H_2O)_2$, $NO^+$ and $O_2^{+\bullet}$ with terpenoid aldehydes and alcohols at 1.5 hPa and 295 K.

| Molecule | M (g/mol) | characterization | $H_3O^+$ | | | | $NO^+$ | | | | | $O_2^{\bullet+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $MH^+$ | $(MH\text{-}H_2O)^+$ | $(MH\text{-}H_2O\text{-}C_4H_8)^+$ | sum | $M^{\bullet+}$ | $(M\text{-}H)^+$ | $(M\text{-}H_2O)^{\bullet+}$ | $(MNO)^+$ | sum | $M^{\bullet+}$ |
| Citronellal[a] | 154 | AC/NS | 25 | 44 | 23 | **92** | 68 | 7 | 13 | - | **88** | **20** |
| Citral[a] | 152 | BC/NS | 41 | 10 | - | **51** | 31 | 28 | - | - | **59** | **15** |
| Myrtenal[a] | 150 | BC/NS | 96 | - | - | **96** | 35 | 28 | - | 18 | **81** | **17** |
| Citronellol[a] | 156 | AC/NS | 49 | 17 | 16 | **82** | 79 | 3 | 12 | - | **94** | **-** |
| Borneol[b] | 154 | BC/S | - | 100 | - | **100** | 33 | 67 | - | - | **100** | **13** |
| Isoborneol[b] | 154 | BC/S | - | 100 | - | **100** | 42 | 58 | - | - | **100** | **7** |
| Linalool[b,c] | 154 | AC/NS | 4 | 56 | 30 | **90** | 5 | - | 53 | - | **58** | **-** |
| Geraniol[c] | 154 | AC/NS | 3 | 62 | 23 | **88** | 37 | 5 | 22 | - | **64** | **2** |
| Nerol[c] | 154 | AC/NS | - | 64 | 31 | **95** | 54 | - | 22 | - | **76** | **4** |
| Menthol[d] | 154 | MC/S | - | 100 | - | **100** | - | 50 | - | - | **50** | **-** |
| Verbenol[b] | 152 | BC/NS | 3 | 42 | - | **45** | 2 | - | 7 | 25 | **34** | **-** |
| Myrtenol[a] | 152 | BC/NS | 7 | 53 | 16 | **76** | 69 | - | - | - | **69** | **-** |
| Carvacrol[b] | 150 | PH | 100 | - | - | **100** | 69 | 13 | 18 | - | **100** | **22** |
| Thymol[b] | 150 | PH | 100 | - | - | **100** | 100 | - | - | - | **100** | **49** |

Table 3: Contributions of the $MH^+$, $(MH\text{-}H_2O)^+$ and $(MH\text{-}H_2O\text{-}C_4H_8)$ reaction pathways, of the $M^{\bullet+}$, $(M\text{-}H)^+$ and $(M\text{-}H_2O)^+$ reaction pathways and of the $M^{\bullet+}$ reaction pathway to the product ion distributions of the reactions of $H_3O^+$, $NO^+$ and $O_2^{\bullet+}$, respectively, with terpenoid aldehydes

and alcohols that have been studied by SIFT-MS. [a] this work, [b] [40], [c] [8], [d] [39], AC: acyclic, MC: monocyclic, BC: bicyclic, S: saturated, NS: non-saturated, PH: phenolic