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REVIEW ARTICLE

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Recent advances in mass spectrometry techniques for atmospheric chemistry research on molecular-level

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Abstract

The Earth's atmosphere is composed of an enormous variety of chemical species associated with trace gases and aerosol particles whose composition and chemistry have critical impacts on the Earth's climate, air quality, and human health. Mass spectrometry analysis as a powerful and popular analytical technique has been widely developed and applied in atmospheric chemistry for decades. Mass spectrometry allows for effective detection, identification, and quantification of a broad range of organic and inorganic chemical species with high sensitivity and resolution. In this review, we summarize recently developed mass spectrometry techniques, methods, and applications in atmospheric chemistry research in the past several years on molecular-level. Specifically, new developments of ion-molecule reactors, various soft ionization methods, and unique coupling with separation techniques are highlighted. The new mass spectrometry applications in laboratory studies and field measurements focused on improving the detection limits for traditional and emerging volatile organic compounds, characterizing multiphase highly oxygenated molecules, and monitoring particle bulk and surface compositions.

KEYWORDS

ambient ionization, chemical ionization, highly oxygenated molecules, isomer separation, organic aerosols, volatile organic compounds

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Abbreviations: AeroFAPA, aerosol flowing ambient-pressure afterglow; AESI, ambient electrospray ionization; AMS, aerosol mass spectrometer; APCI, atmospheric pressure chemical ionization; CCS, collision cross section; CID, collision induced dissociation; CIMS, chemical ionization mass spectrometry; CI-Orbitrap, chemical ionization orbitrap mass spectrometry; DAI, droplet-assisted ionization; DART, direct analysis in real time; EESI, extractive electrospray ionization; EI, electron ionization; ESCI, electrospray chemical ionization; ESI, electrospray ionization; FID, flame ionization detector; FIMR, focusing ion-molecule reactor; GC, gas chromatography; GC-MS, gas chromatography-mass spectrometry; HOMs, highly oxygenated organic molecules; IEPOX, isoprene epoxydiols; IMR, ion-molecule reaction; IMS, ion mobility spectrometry; LC, liquid chromatography; LC-MS, liquid chromatography-mass spectrometry; LTOF, long time-of-flight; nano-DESI, nanospray desorption electrospray ionization; NPF, new particle formation; OA, organic aerosols; OVOCs, oxygenated volatile organic compounds; POA, primary organic aerosols; PS, paper spray; PS-MS, paper spray ionization mass spectrometry; PTR3, PTR-TOF with a tripole reaction chamber; PTR-MS, proton transfer reaction mass spectrometry; PTR-TOF, proton transfer reaction time-of-flight mass spectrometry; RF, radio frequency; SOA, secondary organic aerosols; SSI, sonic-spray ionization; TAG, thermal desorption aerosol gas chromatograph; TD, thermal desorption; TOF-CIMS, chemical ionization time-of-flight mass spectrometry; TOF-MS, time of flight mass spectrometry; VaPI, vacuum-assisted plasma ionization; VOCs, volatile organic compounds; Vocus, PTR-TOF based on a discharge reagent-ion source and focusing ion-molecule reactor; VUV, vacuum ultraviolet.

1 | INTRODUCTION

The chemical characterization of atmospheric gaseous and aerosol constituents has been a well-known challenge due to their extreme complexity caused by the enormous number and distinct properties of inorganic and organic species emitted and formed in the atmosphere. Both biogenic and anthropogenic sources as well as their chemical transformations contribute to the atmospheric complexity, with the chemical and physical properties affecting the Earth's climate, outdoor and indoor air quality, and human health (Boucher et al., 2013; Dockery et al., 1993; Jones, 1999; Merikanto et al., 2009; Watson, 2002). Volatile organic compounds (VOCs) are an important class of atmospheric compounds that could undergo photooxidation in the presence of various atmospheric oxidants, leading to the formation of gas-phase oxidation products with a highly variable and complex functionality and volatility (Claflin et al., 2018; Goldstein et al., 2007; Hallquist et al., 2009; Kroll & Seinfeld, 2008). VOCs also play a central role as precursors in the formation of secondary organic aerosols (SOA), while primary organic aerosols (POA) which are directly emitted into the air make up the other source of atmospheric organic aerosols (OA) (de Gouw & Jimenez, 2009; Hallquist et al., 2009; Jimenez et al., 2009; Zhang et al., 2007). Thus, characterization of the molecular compositions of both the gas- and particle-phase organic species in the atmosphere is of vital importance to understanding the atmospheric chemical kinetics and reaction mechanism for environment assessment and planning.

With the interest of identifying and quantifying organic molecules in the atmosphere, the application of mass spectrometry-based techniques has been popular for many decades. Mass spectrometry techniques accomplish the separation and detection of analyte molecules through three processes of sample introduction, ionization, and mass-to-charge ratio examination, while the advanced innovation in any operation results in the instrument's versatile and comprehensive applications (Laskin et al., 2018). Thus, mass spectrometry can provide qualitative and quantitative analysis for a broad range of chemical species with high sensitivity and short response time (Pratt & Prather, 2012a; Riva, Rantala, et al., 2019). It is widely applied in the identification of unknown chemicals, determination of the elements' isotopic composition in a molecule, and classification of compound structures via fragmentation detection. To elucidate the structures of unknown chemicals, gas chromatography (GC) and liquid chromatography (LC) coupled to mass spectrometers (i.e., GC-MS and LC-MS) emerged as the initial applications of mass spectrometry-based instruments to identify substances in atmospheric gaseous and aerosol mixtures through offline analysis (Covey et al., 1986; Larsen et al., 1996). In these early studies, GC-MS has been widely used to separate and identify hydrocarbon mixtures as well as functionalized organics by employing derivatization techniques (Kawamura et al., 1996; Kubátová et al., 2000; Weschler, 1981; Yokouchi & Ambe, 1985; Yu et al., 1998, 1999), while LC-MS became a powerful technique to analyze relatively polar and high molecular-weight aerosol species (Murray et al., 1994; Willoughby & Browner, 1984; Winkler et al., 1988). With regard to aerosol compositional analysis, progress was made in the early 21st century to allow real-time characterization of atmospheric aerosols by the field-deployable aerosol mass spectrometer (AMS) (Canagaratna et al., 2007; DeCarlo et al., 2006; Tobias et al., 2000). The AMS employs particle size selection and thermal desorption followed by electrode impact (EI) ionization, allowing for quantitively real-time measurements for the element composition, particle mass, and size distributions of atmospheric aerosols (Jayne et al., 2000; Jimenez et al., 2003; Pratt & Prather, 2012b). However, the EI ionization used in AMS is a hard ionization where electrons are accelerated to 70 eV to bombard samples, leading to a high degree of sample fragmentation and thence complicated mass spectra with limited molecular information (Canagaratna et al., 2007; DeCarlo et al., 2006; Tobias et al., 2000). Despite the lack of molecular information, the high time-resolution, near-complete mass coverage, and the potential to infer bulk aerosol characteristic metrics make AMS a popular device in both laboratory studies (Chhabra et al., 2010; Fortenberry et al., 2018; Hu et al., 2017; Kroll et al., 2011; Ng et al., 2011; Sato et al., 2012) and ambient aerosol research (Alfarra et al., 2004; Brüggemann et al., 2015; Chen et al., 2020; DeCarlo et al., 2006; Jimenez et al., 2003; Qi et al., 2019; Takegawa et al., 2005; Ye et al., 2021).

The continued pursuit of real-time and molecular-level characterization of atmospheric constituents led to the development of mass spectrometry instruments based on soft ionization techniques. Chemical ionization mass spectrometry (CIMS) is based on ion-molecule reactions to selectively ionize compounds of interest in the ion-molecule reactor (IMR) (Huey, 2007). As one of the most widely used soft ionization and real-time analysis tool in atmospheric chemistry, CIMS was largely built upon the early development decades ago (Huey, 2007; Viggiano, 1993). In its early versions, the majority of CIMS applications aimed to monitor inorganic compounds (Huey, 2007), except for proton transfer reaction mass spectrometers (PTR-MS), which is a CIMS that uses H_3O^+ as the reagent ion to measure chemically reduced organic compounds with proton affinity higher than water (de Gouw & Warneke, 2007; Hansel et al., 1998). In the early 2010s, the advancement of CIMS with higher sensitivity, better mass resolution, and more versatile reagent ions expanded the measurement capability to a wide range of oxygenated organic species (Bertram et al., 2011; Crounse et al., 2011; Ehn et al., 2012; Lee et al., 2014). In particular, these new developments allowed for a much-improved characterization of moderately to highly oxidized organic species in the atmosphere. While CIMS detects gaseous species, coupling it to aerosol inlets allows for aerosol composition measurements (Eichler et al., 2015; Lopez-Hilfiker et al., 2014; Yatavelli et al., 2012). To measure aerosol constituents, another widely used soft ionization technique is electrospray ionization mass spectrometry (ESI-MS). ESI-MS was usually applied in offline analysis either by itself (Bateman et al., 2010, 2012; De Haan et al., 2009; George et al., 2007; Hastings et al., 2005; Lim et al., 2010; Nguyen et al., 2010) or by coupling with LC (Claeys et al., 2009; Müller et al., 2008; Surratt et al., 2006; Surratt, Kroll, et al., 2007; Warnke et al., 2006; Yasmeen et al., 2011; Zhang et al., 2011). In these studies, the aerosol samples were first collected on membrane filters, followed by solvent extraction procedures and LC-MS analysis. The sample collection, storage, and extraction may lead to undesired artifact reactions (Bateman et al., 2008; Fuller et al., 2014; Hu et al., 2011). To overcome such artifacts, a few methods such as the nanospray desorption electrospray ionization (nano-DESI) and the paper spray (PS) ionization have been explored by directly ionizing molecules from the filter or substrate samples without solvent extraction (Laskin et al., 2018; Liu et al., 2010; Rindelaub et al., 2016; Roach et al., 2010). However, they still require samples to be collected, which loses the time resolution to monitor aerosol formation and evolution. Improvements have been made in the early 2010s to apply soft ambient ionization mass spectrometry in real-time aerosol analysis. Notable examples include the extractive electrospray ionization (EESI) (Doezema et al., 2012; Gallimore & Kalberer, 2013), ambient electrospray ionization (AESI) (Horan et al., 2012), and direct analysis in real-time (DART) (Chan et al., 2013; Chan et al., 2014; Nah et al., 2013). These studies provide valuable insights and guidance for later developments of soft ambient ionization mass spectrometry for aerosol research.

There have been many previous reviews of mass spectrometry methods applied to studying atmospheric chemistry (Blake et al., 2009; Huey, 2007; Laskin et al., 2013, 2018; Sekimoto & Koss, 2021; Yuan et al., 2017; Zhao, 2018). But it is a rapidly growing field where many new analytical techniques, novel designs, and extended applications based on soft ionization mass spectrometry have been published in the recent several years. This review builds on the previous work and summarizes the new mass spectrometry methods and developments in atmospheric chemistry research. We introduce the main principles and workflows of individual mass spectrometry instruments that favor a wider range of measurements for gas-phase compounds and aerosol particles, helping understand the environmental implication of atmospheric chemistry. We further present applications of these techniques in laboratory studies, as well as outdoor and indoor field measurements on a few important research topics. Finally, we discuss several current issues and future developing directions in this field.

2 | NEW SOFT IONIZATION MASS SPECTROMETRY TECHNIQUES AND METHODS

Currently, mass spectrometry characterization of gaseous and aerosol species using soft ionization techniques is a rapidly developing field in atmospheric chemistry for understanding chemical composition. In this section, we introduce several analytical techniques to highlight the improved capabilities for qualitative and quantitative measurements of atmospheric species in the last several years. The major applications and contributions to the atmospheric field of these newly designed mass spectrometry techniques are discussed in the next section.

2.1 | Chemical ionization mass spectrometry: New IMR designs and ionization chemistries

As described above, the development of CIMS has emerged for decades, providing sensitive and rapid measurements for a wide range of atmospheric trace gases. One of the early CIMS techniques applied in the atmospheric chemistry was PTR-MS, which uses H_3O^+ as the reagent ion to ionize analyte molecules through proton transfer reactions (Cappellin et al., 2010; de Gouw & Warneke, 2007; Graus et al., 2010; Kim et al., 2009; Lindinger & Jordan, 1998). CIMS with other reagent ions has also been developed. In particular, numerous studies have reported CIMS measurements using various reagent ions, such as CF_3O^-, $CH_3C(O)O^-$, I^-, SF_6^-, Br^-, NO_3^-, NH_4^+, $C_2H_5OH^+$, NO^+, and so forth to selectively ionize specific molecules through different ion chemistries (Benson et al., 2010; Berry et al., 2018; Bertram et al., 2011; Brophy & Farmer, 2016; Crounse et al., 2011; Ehn et al., 2012; Lawler et al., 2011; Lopez-Hilfiker et al., 2016; Nah et al., 2018; Sanchez et al., 2016; Zaytsev, Breitenlechner, et al., 2019; Zhao, 2018). In many of these development, CIMS with a time-of-flight (TOF) mass analyzer (TOF-CIMS) has been a powerful tool to quantitatively characterize inorganic and organic molecules as low as a few pptv with mass resolving power ($m/\Delta m$) up to 12,000 (Bertram et al., 2011; Krechmer et al., 2018). Figure 1 illustrates the basic configuration of a TOF-CIMS instrument. Ionization occurs in an IMR, where the configuration, residence time, pressure, electric field, and flow rate are optimized for the specific ion chemistry. In this section, we summarize new developments in recent years on IMR hardware designs, ion chemistries to enhance CIMS sensitivities and broaden measurable chemical ranges, and additional capabilities.

2.1.1 | New IMR designs

Vocus

Vocus is a newly developed chemical ionization source consisting of a discharge reagent-ion source and focusing ion-molecule reactor (FIMR) (Krechmer et al., 2018), with the configuration shown in Figure 2A. The reagent ions are produced at the central axis by a low-pressure discharge ion source comprised of two conical surfaces between which a plasma is generated. The produced ions enter through a ring offset from the central axis to ionize the air samples in the FIMR. The FIMR includes a quadrupole mounted outside of a glass tube with a resistive coating to build an inside axial electric field of a radio frequency (RF) quadrupole, focusing ions into a narrow beam on the central axis to enhance the sensitivity. Comparing with a traditional PTR-TOF, a Vocus-equipped PTR-TOF is ~19 times more sensitive for many VOCs (Figure 3A). According to ambient measurement comparison between a Vocus-equipped PTR-TOF and a traditional PTR-TOF, Vocus also showed much higher detection precision due to the improved sensitivity and mass spectral resolution, which are paramount among other gas-phase measurement techniques (Koss et al., 2020; Riva, Rantala, et al., 2019; Wang, Mehra, et al., 2020; Wu et al., 2021; Zaytsev, Breitenlechner, et al., 2019). It is also worth mentioning that Vocus exhibits an almost independent sensitivity on the relative humidity of the sample air owing to the high water vapor mixing ratio in the FIMR, in contrast to conventional PTR-MS instruments (Figure 3B). The response times of Vocus-equipped PTR-TOF are about an order of magnitude shorter than a traditional PTR-TOF (Krechmer et al., 2018).

PTR3

PTR3 is developed based on a standard PTR-TOF equipped with a new center-sampling inlet and an innovative IMR design (Breitenlechner et al., 2017). A corona discharge ion source is operated in PTR3 followed by a source drift area (Figure 2B). The drift area is split into two regions, where chemical ionization gas and humidified nitrogen gas carrier are separately inserted and transported to a tripole IMR chamber. The design of splitting flow decreases the byproducts by preventing the formation of interfering primary ions and radicals. The tripole supplied with a RF voltage decouples the directions of sample gas flow (axial) and high-energy

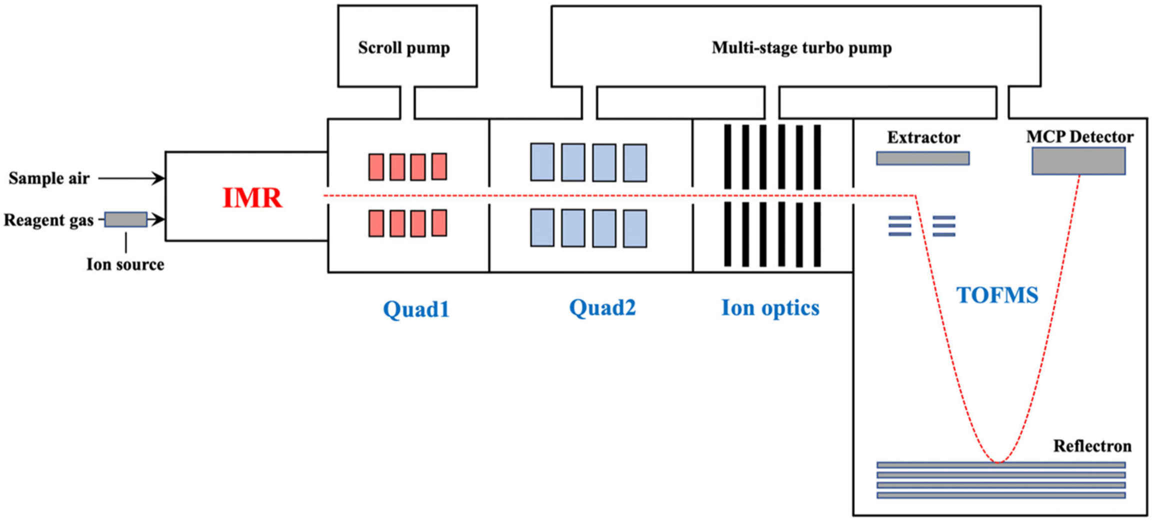

FIGURE 1 An illustrative diagram of the CIMS configuration. CIMS, chemical ionization mass spectrometry. [Color figure can be viewed at wileyonlinelibrary.com]

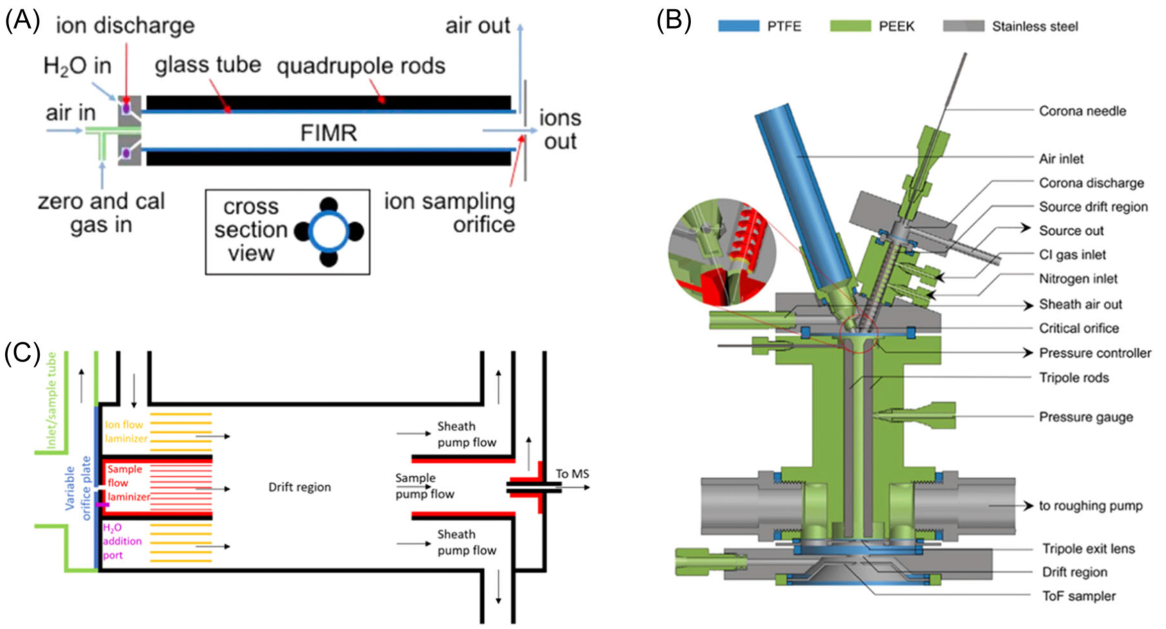

FIGURE 2 (A) Design of the Vocus consisting of a discharge reagent-ion source and a focusing ion−molecule reactor (FIMR). Reproduced with permission Krechmer et al. (2018). Copyright 2018 American Chemical Society. (B) Schematic representation of the PTR3 front part. Reproduced with permission Breitenlechner et al. (2017). Copyright 2017 American Chemical Society. (C) Schematic of the new coaxial, low-pressure IMR design to reduce wall interaction. Black lines represent stainless steel surfaces, green and blue lines represent PTFE Teflon, and red/yellow lines represent FEP or PFA Teflon. Reproduced with permission Palm et al. (2019). Copyright 2019 Palm et al. [Color figure can be viewed at wileyonlinelibrary.com]

collisions (radial). As a result, the reaction time, pressure, and reduced electric field strength of PTR3 are independent of each other, leading to the possible improvement of operational parameters. Another improvement is the inlet design which minimizes wall loss by controlling symmetrical exhaustion of the sheath gas around the core flow. The new designs of PTR3 extend the reaction time 30 times longer and the pressure 40 times higher compared to the standard PTR-TOF. After the pressure drops in the drift region, the gas flow is guided to a long TOF (LTOF) mass analyzer, further improving the resolving power for better separation of isobaric ions (Lehtipalo et al., 2018). Calibration tests of different compound classes showed a result of up to 18,000 counts per second (cps)/ppbv at a mass resolving power ($m/\Delta m$) of >8,000, which exhibits a much better performance than the standard PTR-TOF (Koss et al., 2018; Pagonis, Sekimoto, et al., 2019). Further, Piel et al. (2021) introduced an extended volatility range inlet coupled with PTR3 to improve its time response by inhibiting the surface interactions of low volatility analytes within the gas inlet and the tripole IMR chamber (Piel et al., 2021). Despite the promising features of PTR3, Holzinger et al. (2019) suggested that it tends to form larger water clusters and deprotonation species by comparing the performances of different PTR instruments in field work (Holzinger et al., 2019).

IMR design to reduce wall interactions

Reducing the interactions between relatively low-volatility analytes and IMR inner walls helps avoid sample loss and reduce response delay in CIMS measurements due to temporary adsorption of the analytes on inlet surfaces. In the study by Palm et al., a new coaxial, low-pressure IMR (Figure 2C) was designed to minimize wall loss meanwhile improving sensitivity of CIMS (Palm et al., 2019). The new design includes: (1) removing as many wall surfaces as possible and having any necessary wall surfaces be constructed from materials such as perfluoroalkoxy (PFA) Teflon, which have been reported to have minimized interactions with analytes (Deming et al., 2019; Liu, Deming, et al., 2019; Pagonis et al., 2017); (2) making the distance between analyte and surfaces as large as possible by controlling the analyte flow into a coaxial sheath, similar to previous IMR designs for the NO_3^- reagent ion (Jokinen et al., 2012; Massoli et al., 2018); (3) exhausting the desorbed compounds from wall surfaces by pumping a sheath flow radially outside of a sample flow; and (4) maintaining IMR pressure constant within the range of 200 to 760 Torr even on an aircraft platform through the design of a variable orifice on the upstream side of the IMR (Lee et al., 2018). The demonstration used I^- as the reagent ion but may be applicable to other reagent ions. As shown in Palm

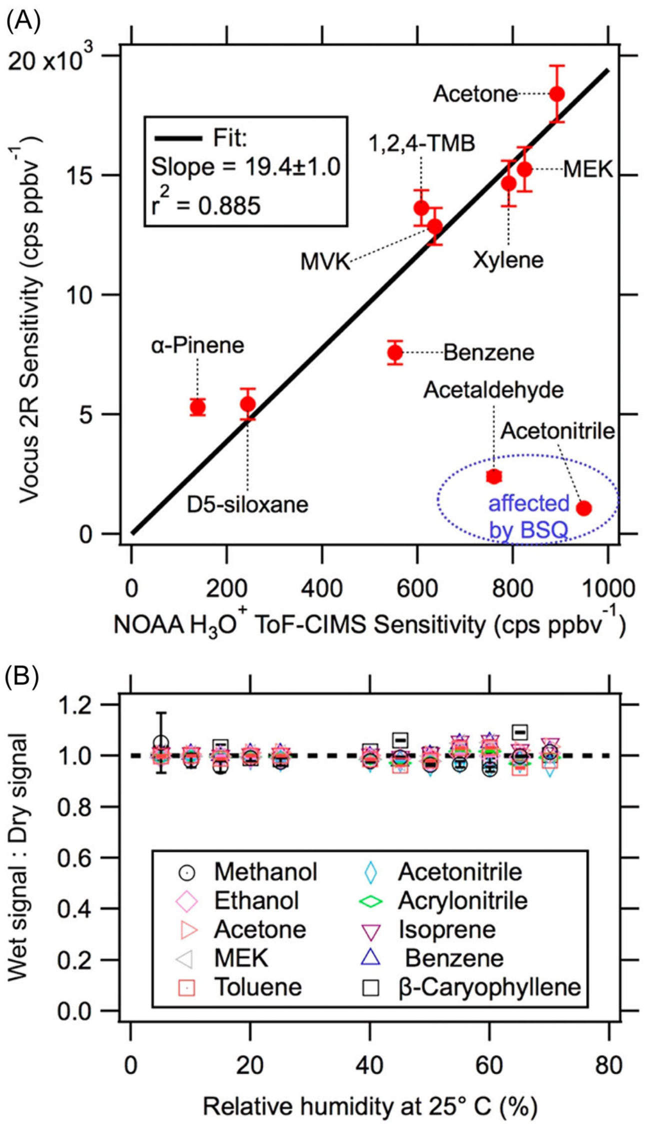

FIGURE 3 (A) Comparison of sensitivities between the vocus PTR-TOF and NOAA PTR-TOF. Vocus sensitivities were determined during the ACTRIS-PICAB field campaign and represent an average over 24 h (12 separate calibrations). Error bars represent the 1σ standard deviation. (B) Humidity dependence of the vocus PTR-TOF product ion signals. Reproduced with permission Krechmer et al. (2018). Copyright 2018 American Chemical Society. NOAA, National Oceanic and Atmospheric Administration; PTR-TOF, proton transfer reaction time-of-flight mass spectrometry. [Color figure can be viewed at wileyonlinelibrary.com]

et al., I^- is introduced at the front of the drift region in the IMR and it ionizes analytes in the center of the drift region, such that less than 4% of the analytes have interactions with wall surface according to diffusion calculations. As a result, the delay time of CIMS coupling with this IMR design is 3–10 times lower than previous CIMS versions, as illustrated in Figure 4.

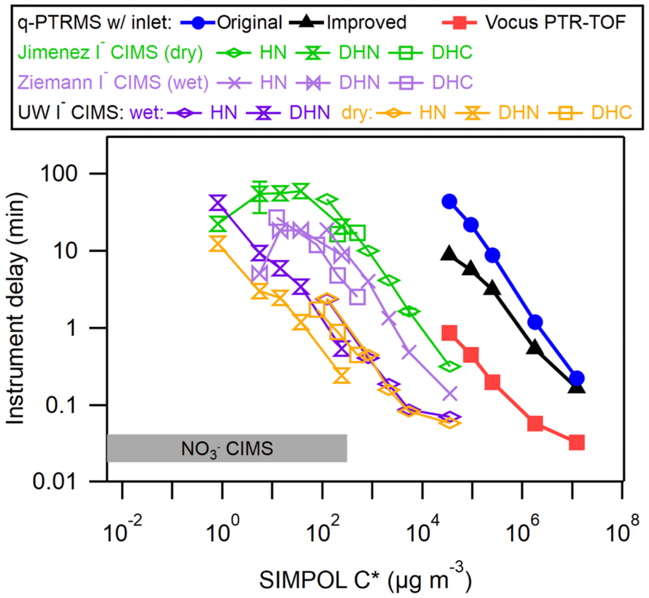

FIGURE 4 Delay times for a variety of organic molecules as a function of saturation vapor concentrations (C*, μg m^{-3}), compared with previous IMR designs including a quadrupole PTR-MS, Vocus PTR-TOF, and several I^--CIMS instruments with different IMRs. The delay time in a NO_3^--CIMS is also shown for comparison. Reproduced with permission Palm et al. (2019). Copyright 2019 Palm et al. CIMS, chemical ionization mass spectrometry; IMR, ion-molecule reactor; PTR-MS, proton transfer reaction-mass spectrometry. [Color figure can be viewed at wileyonlinelibrary.com]

2.1.2 | Ionization chemistries in CIMS

CIMS has been widely used in in-situ measurements of a variety of atmospheric trace gases and aerosol species due to its excellent selectivity and sensitivity. The most common reagent ions used with CIMS include H_3O^+, NO^+, $C_6H_6^+$, $C_2H_5OH^+$, NH_4^+, and protonated amines in the positive ion mode, and I^-, $CH_3C(O)O^-$, CF_3O^-, SF_6^-, Br^-, and NO_3^- in the negative ion mode. It is essential to choose an appropriate reagent ion for CIMS to selectively and effectively ionize one or several targeted classes of compounds from a complex system. A comparison of the types of ion chemistry and targeted species by different reagent ions is listed in Table 1. Here, we focus on describing new ion chemistries studied in recent years which allow for broader applications of CIMS in identification and quantification of molecules relevant to atmospheric chemistry.

For all types of ion chemistry, the reagent ions are created from reagent gases by a radioactive ion source (e.g., ^{210}Po and 10 MBq Am), discharge (Breitenlechner et al., 2017; Krechmer et al., 2018), X-rays (Bertram et al., 2011; Bianchi et al., 2019; Riva et al., 2020), or a vacuum ultraviolet (VUV) ion source (Breitenlechner

TABLE 1 Summary of common CIMS reagent ions and the corresponding ion chemistries and detectable compounds.

Reagent ion	Source gas	Ion source	IMR/mbar/ms	Primary ion chemistry	Detected compounds	References
H_3O^+	Water vapor	Hollow cathode discharge	Ring-stack drift tube /~2/~0.1	$H_3O^+ + M$ $\rightarrow [M{+}H]^+ + H_2O$	Compounds with proton affinity larger than water (e.g., majority of VOCs)	de Gouw et al. (2003); Hansel et al. (1995)
		Glow discharge	Focusing IMR /~1/~0.1			Krechmer et al. (2018)
		Corona discharge	Tripole/80/3			Breitenlechner et al. (2017)
NO^+	Ultrahigh-purity air	Hollow cathode discharge	Ring-stack drift tube /~2/0.1–0.2	$NO^+ + M$ $\rightarrow M^+\ NO$ $\rightarrow [M{-}H]^+ + HNO$ $\rightarrow [M \rightarrow + NO]^+$	Compounds with low ionization energy or hydride transfer reaction enthalpy, otherwise favoring adduct formation (e.g., carbonyl species, small branched alkenes, some alkanes)	Karl et al. (2012); Koss et al. (2016)
$(C_6H_6)_2{}^+$	Benzene	^{210}Po	Canonical IMR/70/100	$(C_6H_6)_2{}^+ + M$ $\rightarrow M^+ + 2{\bullet}C_6H_6$ $\rightarrow [M{+}(C_6H_6)_2]^+$ $\rightarrow [M + C_6H_6]^+ + C_6H_6$	Compounds with ionization energy lower than benzene, and with $C_6H_6{}^+$ affinity[a] larger than benzene (e.g., dimethyl sulfide, isoprene, terpenes)	Kim et al. (2016); Lavi et al. (2018)
$(C_2H_5OH)_nH^+$	Ethanol	^{241}Am	Transverse IMR/1000/~7	$(C_2H_5OH)_nH^+ + M$ $\rightarrow [M{+}(C_2H_5OH)_{n-1}H]^+ + C_2H_5OH$ $\rightarrow [M + H]^+ + nC_2H_5OH$	Compounds with proton affinity larger than ethanol (e.g., dimethyl sulfoxide, ammonia and amines)	Nowak et al. (2002)
		^{210}Po	Canonical IMR/20-200/~0.1			Berry et al. (2018); Yu and Lee (2012)
$NH_4{}^+$	N_2/H_2O mixture	hollow cathode discharge	Ring-stack drift tube/2.3/~0.5	$NH_4{}^+ + M$ $\rightarrow [M + NH_4]^+$ $\rightarrow [M + H]^+ + NH_3$	Compounds with proton affinities higher than ammonia; compounds with high binding enthalpies to $NH_4{}^+$ (e.g., some VOCs, OVOCs, HOMs, amines, and $RO_2{}^\bullet$)	Canaval et al. (2019)
	NH_3		Ring-stack drift tube/~2/~0.1			Müller et al. (2020)
$NH_4{}^+{\bullet}H_2O$	NH_3/H_2O mixture	Glow discharge	Focusing IMR /~3/0.2	$NH_4{}^+{\bullet}H_2O + M$ $\rightarrow [M + NH_4]^+ + H_2O$	Compounds with $NH_4{}^+$ affinity[a] larger than H_2O (e.g., monoterpenes, majority of OVOCs)	Khare et al. (2022); Xu et al. (2022a)
		Corona discharge	Tripole/50-70/3			Zaytsev, Breitenlechner, et al. (2019)
$C_3H_7NH_3{}^+$	n-propylamine	^{241}Am	Flow tube IMR/1000/200-300	$C_3H_7NH_3{}^+ + M$ $\rightarrow [M + C_3H_7NH_3]^+$	HOMs, Criegee Intermediate, $RO_2{}^\bullet$	Berndt et al. (2018b)

(Continues)

TABLE 1 (Continued)

Reagent ion	Source gas	Ion source	IMR/mbar/ms	Primary ion chemistry	Detected compounds	References
I^-	CH_3I	^{210}Po	Canonical IMR/ 90/~120	$I^- + M$ $\rightarrow [M + I]^-$	Compounds with high binding enthalpies to I^- (e.g., HONO, N_2O_5, OVOCs, HOMs, $RO_2^{\bullet}$)	Lee et al. (2014)
		VUV	Flow tube IMR /20-50/10-20			Ji et al. (2020)
		VUV	FIMR/9/30			Breitenlechner et al. (2022)
Br^-	CF_3Br	^{210}Po	Canonical IMR/ 100/70	$Br^- + M$ $\rightarrow [M + Br]^-$	Compounds with high binding enthalpies to Br^- (e.g., OVOCs, HOMs, $HO_2^{\bullet}$, $RO_2^{\bullet}$, halogen species, and sulfuric acid)	Sanchez et al. (2016)
	CH_2Br_2	X-ray	MION/1000/30			Rissanen et al. (2019)
$CH_3C(O)O^-$	Acetic anhydride	^{210}Po	Flow tube IMR/ 43/~80	$CH_3C(O)O^- + M$ $\rightarrow [M + CH_3C(O)O]^-$ $\rightarrow [M\text{–}H]^- + CH_3C(O)OH$	Compounds with gas-phase acidity larger than acetic acid (e.g., majority of organic acids, HOMs, and $RO_2^{\bullet}$)	Veres et al. (2008)
			Canonical IMR/20-100/100			Bertram et al. (2011)
NO_3^-	HNO_3	^{241}Am	Flow tube IMR/ 1000/200	$NO_3^-\bullet(HNO_3)_n + M$ $\rightarrow [M + NO_3]^- + (HNO_3)_n$ $\rightarrow [M\text{–}H + HNO_3]^{-}$[b] $+ (HNO_3)_n$	Compounds with gas-phase acidity larger than HNO_3 or high binding enthalpies to NO_3^- (e.g., sulfuric acid, nitroaromatics, HOMs, and $RO_2^{\bullet}$)	Eisele and Tanner (1993); Jokinen et al. (2012)
CF_3O^-	CF_3OOCF_3	^{210}Po	Transverse IMR/ 35/~1	$CF_3O^- + M$ $\rightarrow [M+CF_3O]^-$ $\rightarrow [M\text{–}H+HF]^{-}$[b] $+ CF_2O$	Compounds with large gas-phase acidity or high binding enthalpies to CF_3O^- (e.g., organic acids, hydroperoxides, and nitrates, H_2O_2, HNO_3, HONO, HCN, SO_2)	Allen et al. (2022); Crounse et al. (2006)
SF_6^-	SF_6	^{210}Po	Flow tube IMR/ ~13/5–10	$SF_6^- + M$ $\rightarrow [M\text{--}H+HF]^{-}$[b] $+ SF_5$ $\rightarrow [M\text{–}H]^- + HF + SF_5$	Inorganic compounds and organic acids	Nah et al. (2018)

[a] As analogous to proton affinity, we define NH_4^+ affinity and $C_6H_6^+$ affinity as the negative of the enthalpy change in the reaction between analyte and NH_4^+ or $C_6H_6^+$, respectively.

[b] The "M–H" in these ion formulas indicates acid deprotonation.

et al., 2022; Ji et al., 2020). The reagent ions react with analytes in the IMR. The IMR operation conditions and configurations are designed for specific reagent ions and analyte molecules. The IMR can be held at atmospheric pressure or a reduced pressure. For instance, protonated amine and NO_3^- ion chemistries were often carried out under atmospheric pressure while most other ion chemistries require varied levels of low-pressure (2–200 mbar). The IMR also has a variety of designs. For example, the standard IMR used for I^-, $CH_3C(O)O^-$, SF_6^-, Br^-, and so forth introduces the reagent ions perpendicularly with the mass spectrometer inlet nozzle and orthogonally to the sample flow with a mixing time ~100–200 ms (Bertram et al., 2011). The CF_3O^--CIMS IMR was designed in a transverse fashion with the reagent ions accelerated toward the inlet orifice by the electric field and the sample flow in a perpendicular direction, at a much shorter mixing time ~1 ms (Crounse et al., 2006). The shorter reagent ion-molecule mixing time results in the reaction in the kinetic limited regime. Another important factor of IMR design is to minimize the analyte-wall interaction. For example, for the IMR in NO_3^--CIMS targeting at low vapor pressure analytes, the reagent ions in a sheath flow are guided and accelerated via an electric field to meet the samples in parallel to minimize the wall interaction (Bianchi et al., 2019). After the IMR, the ionized samples are transmitted through the ion optics. In the example shown in Figure 1, the charged ions enter a small segmented quadrupole with tunable frequency and amplitude to be effectively guided, focused, and cooled, followed by a second big segmented quadrupole stage housed at nearly vacuum condition (Yuan et al., 2016). Weakly bounded ion-molecule clusters could experience collisional dissociation caused by the voltage difference between the two quadrupole regions (Aljawhary et al., 2013; Bertram et al., 2011; Huey, 2007; Lopez-Hilfiker et al., 2016). Finally, the primary beam travels through a series of DC optics to be further focused and accelerated before entering the mass analyzer.

With the above-described generic CIMS configuration, many ion chemistries can be employed (Table 1). The hydronium ions (H_3O^+) can ionize molecules with proton affinity higher than water, yielding protonated ion clusters via proton-transfer reactions in the drift tube. The reagent ion NO^+ is able to ionize VOCs through three different ionization mechanisms, charge transfer, hydride abstraction, and cluster formation, dependent on the reaction enthalpy of compound molecules (Koss et al., 2016). The proton- or hydride-transfer reactions are more favorable with a more negative proton- or hydride-transfer reaction enthalpy, otherwise the formation of $[VOC + NO]^+$ adducts occurs. Benzene cluster cations have been used to detect dimethyl sulfide and terpenes by forming adducts (Kim et al., 2016; Lavi et al., 2018). The $[C_2H_5OH + H]^+$ clustering process is typically applied to detect dimethyl sulfoxide, a series of non-methane hydrocarbons, and amines (Benson et al., 2010; Berry et al., 2018; Nowak et al., 2002). The NH_4^+ ionization can detect a wide range of organic and inorganic species, including ketones, alcohols, peroxy radicals ($RO_2^•$), and amines (Canaval et al., 2019; Hansel et al., 2018; Müller et al., 2020; Xu, et al., 2022b; Zaytsev, Breitenlechner, et al., 2019; Zhu et al., 2018). The protonated amine ion chemistry (e.g., *n*- or *tert*-butylamine or diethylamine) has been more specifically used to measure highly oxygenated molecules (HOMs) and $RO_2^•$ (Berndt et al., 2017; Berndt, Mentler, et al., 2018; Berndt, Scholz, et al., 2018). Among the negative reagent ions, I^- and Br^- have been widely used to measure atmospheric relevant inorganic and organic species, including halogen-containing species, moderately oxygenated VOCs (OVOCs), HOMs, and $RO_2^•$ (Lawler et al., 2011; Lee et al., 2014; Priestley et al., 2021; Rissanen et al., 2019; Sanchez et al., 2016, 2021). $CH_3C(O)O^-$ can ionize inorganic and organic acids that are more acidic than acetic acid as well as HOMs (Berndt, Richters, et al., 2016; Bertram et al., 2011; Hansel et al., 2018). NO_3^- is also a well-known reagent ion to measure HOMs by forming adducts (Ehn et al., 2012, 2014; Rissanen et al., 2014, 2015), but may have distinct sensitivities for different HOMs in comparison to $CH_3C(O)O^-$ (Berndt, Richters, et al., 2016). CF_3O^- has been used to detect OVOCs, organic hydroperoxides, and nitrates through ion-molecule clustering or fluoride transfer reactions (Crounse et al., 2006; Paulot et al., 2009; Vasquez, Crounse, et al., 2020). SF_6^- ionizes some inorganic compounds and organic acids through proton or fluoride transfer reactions (Huey et al., 1995; Nah et al., 2018; Slusher et al., 2001). As described here, the same class of organic compounds can be detected by several different ion chemistries. Figure 5 shows a comparison between several popular ion chemistries in the detection suitability of α-pinene oxidation products with varied molecular composition (Riva, Rantala, et al., 2019). Depending on the volatility, stability, and degree of oxygenation, the detection suitability for different ion chemistries also varies.

2.1.3 | Extended capabilities of CIMS

Switchable reagent ion CIMS

For both laboratory research and field studies, the selective nature of CIMS may inhibit comprehensive measurements of a wide range of chemicals of interest.

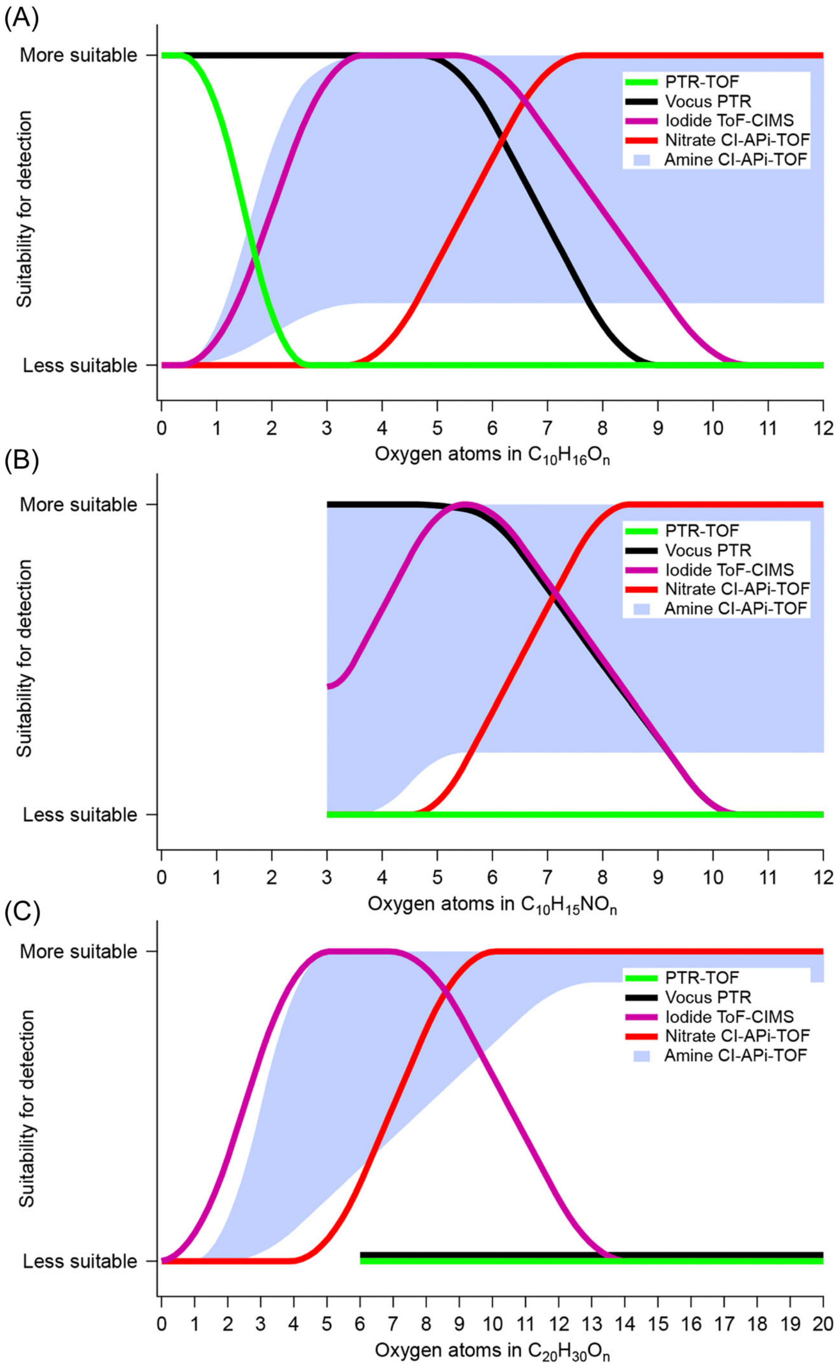

FIGURE 5 Estimated detection suitability of the different CIMS techniques for α-pinene and its oxidation products, plotted as a function of the number of oxygen atoms. Each panel symbolizes a compound group: (A) monomers, (B) organic nitrate monomers, and (C) dimers. Reproduced with permission Riva, Rantala, et al. (2019). Copyright 2019 Riva et al. CIMS, chemical ionization mass spectrometry. [Color figure can be viewed at wileyonlinelibrary.com]

To overcome this limitation, a few studies have developed a switchable reagent ion (SRI, also known as selective reagent ion) approach to allow two or more reagent ion chemistries alternate during CIMS measurements. For example, the SRI-PTR-MS (or SRI-PTR-TOF) that enables switching between H_3O^+, NO^+, and $O_2{}^+$ has been used to more comprehensively characterize VOCs for years (Jordan et al., 2009; Smith & Španěl, 2005; Sulzer et al., 2013). In addition, Brophy and Farmer developed an SRI-CIMS to switch between I^- and $CH_3C(O)O^-$ reagent ions to measure compounds across a large mass range and focus on specific species (Brophy & Farmer, 2015). Based on the development of PTR3, more recently, Zaytsev et al. introduced a PTR3-based SRI-CIMS that can switch between H_3O^+ and $NH_4{}^+$ reagent ion chemistries within 2 min (Koss et al., 2020; Zaytsev, Koss, et al., 2019). Rissanen et al. developed a Multi-scheme chemical ionization inlet (MION) for fast switching between Br^- and $NO_3{}^-$, allowing multiple consecutive chemical ionization in fast repetition at atmospheric pressure (Rissanen et al., 2019). The ion chemistry scheme can be changed within a second timescale by simply switching low-voltage settings, and the ion-molecule reaction time is adjustable by changing the length between two ion sources. Breitenlechner et al. recently coupled a VUV ion source to a commercial Vocus PTR-TOF in which the discharge ion source is replaced with two VUV lamps (Breitenlechner et al., 2022). Different from the glow discharge ion source, the VUV ion source can efficiently generate both positive and negative reagent ions, allowing for the switchable polarities to access different ion chemistries such as the original H_3O^+-PTR-MS and the widely used I^--CIMS. Meanwhile, the VUV ion source not only reduces ion fragmentation but also inhibits the sputtering processes of fast ions which contributes to longer lifetime of the ion source region.

Thermal desorption-based CIMS for aerosol analysis

Although CIMS was originally designed for real-time analysis of atmospheric trace gases, its coupling with thermal desorption-based inlets allows for measurements of chemical composition in the particle phase. One commonly used aerosol inlet in the past few years is the Filter Inlet for Gases and Aerosols (FIGAERO), which simultaneously sample gas species and collects aerosol particles on a Teflon filter followed by temperature-ramped thermal desorption to vaporize particle-phase chemicals into the gas phase (Lopez-Hilfiker et al., 2014). The relatively short sampling time (hourly) due to its high sensitivity allowed the usage of FIGAERO-CIMS in the laboratory settings and real atmosphere (Lopez-Hilfiker et al., 2015; Mohr et al., 2017; Zhang et al., 2018). Without filter collection, real-time particle-phase composition analysis can be achieved by direct thermal desorption, though the detection limit is degraded than the filter-based method (Zhao, Yang, et al., 2020). Two common examples of such inlets are described below. The first one is the "chemical analysis of aerosol online" (CHARON) inlet system for online chemical characterization of semi-volatile submicron particles (Eichler et al., 2015). The CHARON particle inlet consists of a gas phase denuder which removes gas-phase organic compounds, an aerodynamic lens which concentrates aerosols in the subsampling flow with the combination of an inertial sampler, and a thermal desorption unit which operates at a reduced pressure of ~10 mbar and a constant heating temperature in the range of 50–250°C for particle volatilization before the chemical analysis by PTR-MS (Eichler et al., 2015; Pagonis et al., 2021; Piel et al., 2021). The CHARON-PTR-MS has been successfully used for detection of organic compounds and ammonium constituents in aerosol particles (Eichler et al., 2015; Leglise et al., 2019; Piel et al., 2021). The second example is the Vocus inlet for aerosols (VIA), recently introduced by Häkkinen et al. for measurements of particle-phase HOMs by coupling to NO_3^--CIMS (Häkkinen et al., 2022; Zhao, Häkkinen, et al., 2022). Similar to the CHARON inlet, the VIA first passes aerosols samples through an activated charcoal gas denuder to remove gas-phase constituents (Zhao, Häkkinen, et al., 2022). Then the remaining aerosol species are evaporated at a chosen temperature between 25°C and 300°C by a Sulfinert-coated stainless-steel thermal desorption tube under ambient pressure (Avery et al., 2023; Häkkinen et al., 2022). A dilution flow of clean air is introduced to cool down the samples before they enter the IMR.

CIMS with Orbitrap as the mass analyzer

Chemical ionization coupled to an Orbitrap mass spectrometry (CIMS-Orbitrap) has become a new technique among high-resolution CIMS instruments in atmospheric chemistry (Riva, Ehn, et al., 2019; Zuth et al., 2018). Orbitrap is an ion trap mass analyzer essentially consisting of three electrodes (Makarov, 2000; Zubarev & Makarov, 2013). Two outer barrel-like electrodes face each other and are electrically isolated, held together with a coaxial inner spindle-like central electrode. A strictly linear electric field is generated when the voltage is applied to the outer and the central electrodes, while ions are trapped to the central electrode by the radial electric component. Ions cycle around the inner electrode by balancing the electrostatic attraction and the centrifugal force of tangential movements. Meanwhile, the axial electric component forces ions moving back and forth along the axis. As a result, the trajectories of ions inside the trap are nearly circular spiral. Ions with different mass-to-charge ratios move with the same axial frequency but different rotational frequencies, thus ions of interest with a specific mass-to-charge ratio could be selected and guiled to the analyzer. Compared to TOF-CIMS, CI-Orbitrap has much higher mass resolving power ($m/\Delta m$ of 140,000), and has been proved to be able to measure VOCs and $RO_2^\bullet$ at atmospherically relevant concentrations (Riva et al., 2020). Direct mass spectra comparisons of CI-Orbitrap with typical TOF-CIMS are shown in Figure 6, demonstrating the superior peak identification and formula assignment using CI-Orbitrap. A recent study showed improved sensitivity in measuring the OVOC with low concentrations down to 5×10^4 molecules cm^{-3} as well as the number of detected compounds above the 50% sensitivity threshold by optimizing different governing parameters of the chemical ionization Orbitrap Fourier transform mass spectrometry (Cai et al., 2022). Moreover, its ability to

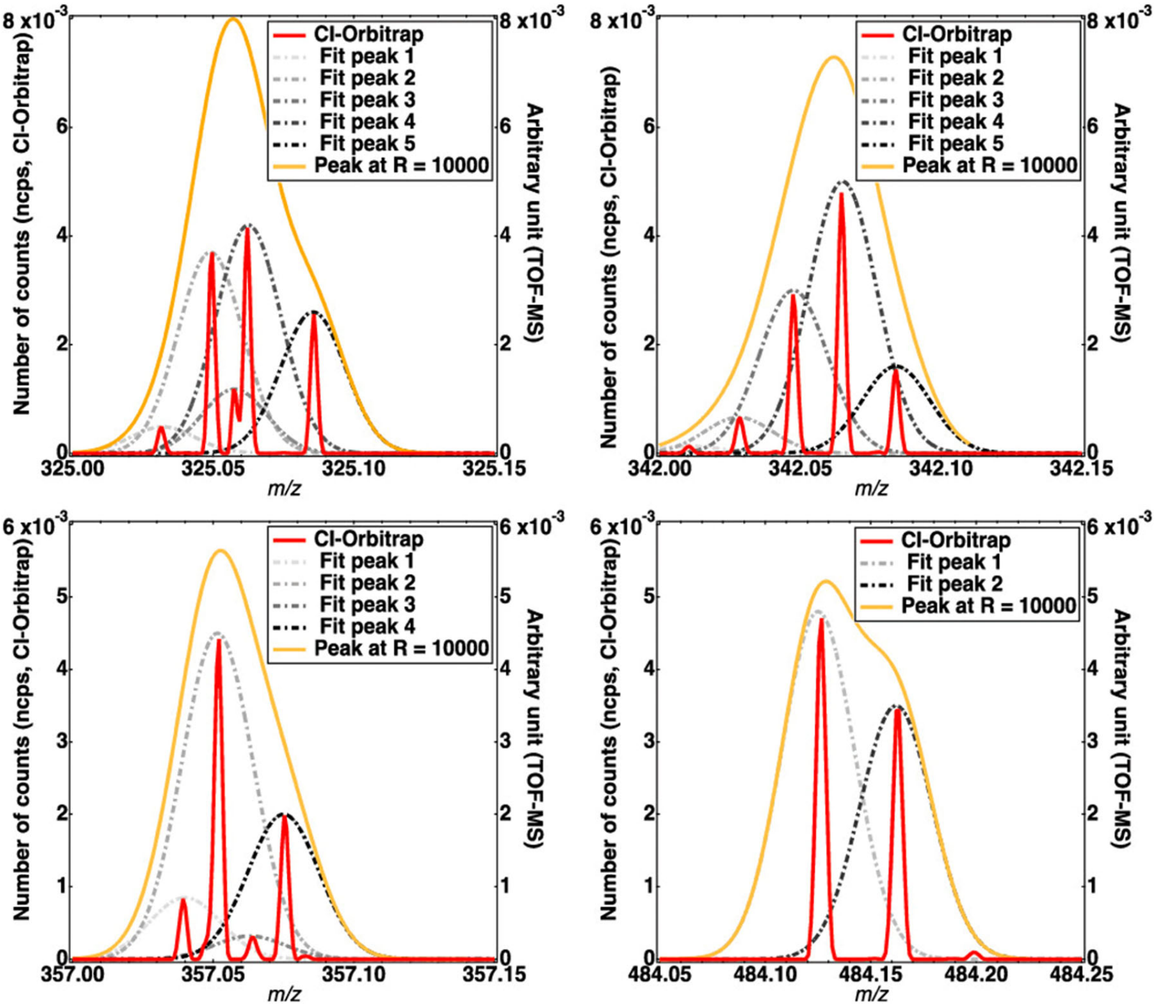

FIGURE 6 Mass spectra (red) of different HOM, at *m/z* 325, 342, 357, and 484, measured by a NO_3-CI-Orbitrap during limonene ozonolysis. The orange trace represents the spectrum that would be observed using an instrument with mass resolving power of 10,000. Dashed lines stand for the fits of individual ions. The TOF-MS signals represent synthetic data using arbitrary units and do not aim at matching the surface area measured using the CI-Orbitrap. Reproduced with permission Riva, Rantala, et al. (2019). Copyright 2019 American Chemical Society. HOM, highly oxidized molecule; TOF-MS, time of flight mass spectrometry. [Color figure can be viewed at wileyonlinelibrary.com]

use tandem mass spectrometry analysis allows for structural analysis of target molecules, leading to its potential applications in detecting trace-level components of atmospheric complex chemical mixtures.

2.2 | Ambient ionization techniques designed for aerosol analysis

Ambient ionization usually refers to ionization methods in which molecules are ionized in their native environment, typically for condensed-phase samples in air. In the past, many ambient ionization mass spectrometry techniques were employed based on physical-chemical processes such as laser ablation, thermal desorption, and vibrational excitation, enabling analysis of environmental samples (Feider et al., 2019). In atmospheric chemistry, especially for aerosol research, ambient ionization mass spectrometry techniques are used to ionize molecules in aerosols directly in the air, allowing for nearly real-time sampling and the subsequent analysis for aerosol molecular chemical composition without sample collection, preparation, or extraction (Brüggemann et al., 2015; Feider et al., 2019). Recently, real-time and direct aerosol mass spectrometry analysis with soft ambient ionization has made large progress, such as EESI and DART. The key advances of these soft ambient ionization mass spectrometry techniques are summarized in this section.

2.2.1 | ESI-based techniques

EESI-MS

ESI is a well-known technique that uses electrospray to ionize polar molecules under high voltage and transfer the ions from solution phase into the gas phase as the sprayed microdroplets evaporate. As described in the Introduction, the early applications of ESI-MS in aerosol research were mostly through direct infusion of liquid samples after aerosol collection and extraction (Reemtsma et al., 2006; Zhang et al., 2011). The EESI technique combines ESI with online aerosol measurement as the simplified configuration shown in Figure 7A (Chen et al., 2006; Doezema et al., 2012; Gallimore & Kalberer, 2013; Gallimore et al., 2017; Lopez-Hilfiker et al., 2019). Gas-scrubbed aerosol samples can be directly introduced into the EESI inlet, where the sample flow collides with a charged and stable solvent electrospray plume to be extracted into the bulk electrospray, which is generated by the potential difference between an ESI probe and the mass spectrometer inlet (Figure 7A). The electrospray solution is usually doped with a strong ionic compound such as sodium iodide to promote ionization by providing stronger adducts and reference signals for mass calibration (Pospisilova et al., 2021; Zhao, Chan, et al., 2017). The angle and the distance between aerosol sample flow, the ESI probe, and the mass spectrometer inlet could be optimized for best ion signals. The aerosol molecules are ionized and ejected into the gas phase by the rapid evaporation of electrospray solvent through the Coulomb explosion mechanism (Kebarle & Peschke, 2000). Then aerosol samples enter a heated ion capillary to ensure the evaporation of electrospray droplets during the ~1 ms capillary transit before mass spectrometry analysis. Finally, the generated molecular ions are detected by a mass analyzer to obtain real-time aerosol composition measurements at a near-molecular level (Lee et al., 2020). The reported detection limit using recently developed sensitive EESI-MS is typically on the order of 1–10 ng m^{-3} in 5 s (Gallimore et al., 2017; Lopez-Hilfiker et al., 2019).

EESI-MS provides a controlled ionization scheme to avoid the reliance of the conventional methods on thermal desorption, fragmentation causing by hard ionization or separated collection-extraction-analysis stages (Brown et al., 2021; Pospisilova et al., 2020; Surdu et al., 2021). Although EESI-MS showed significantly different sensitivity towards different organic compounds by up to a factor of 30, the ion signals of a respective compound exhibit a linear response to compound mass over several orders of magnitude, highlighting the potential benefits of EESI to quantify atmospheric aerosols (Gallimore et al., 2017; Lopez-Hilfiker et al., 2019). According to ambient measurements, potential factors affecting the instrument response, including the soluble inorganic matric, varied water vapor, and largely varied particle sizes, only slightly disturb the aerosol detection and analysis (Gallimore et al., 2017; Lopez-Hilfiker et al., 2019; Pagonis et al., 2021). With the increasing needs of using soft ambient ionization mass spectrometry methods to perform real-time measurements and quantitive characterization of aerosol compositions at the molecular level, EESI-MS is expected to provide comprehensive analysis of atmospheric aerosol species (Hems et al., 2021; Huang et al., 2019). For example, EESI-MS is promising as an alternative of the offline LC-ESI-MS to measure key atmospheric SOA tracers such as organosulfates in real-time (Brüggemann et al., 2020). EESI-MS also exhibits a quantitative capability to monitor the dynamic concentrations of individual compounds in mixed organic-

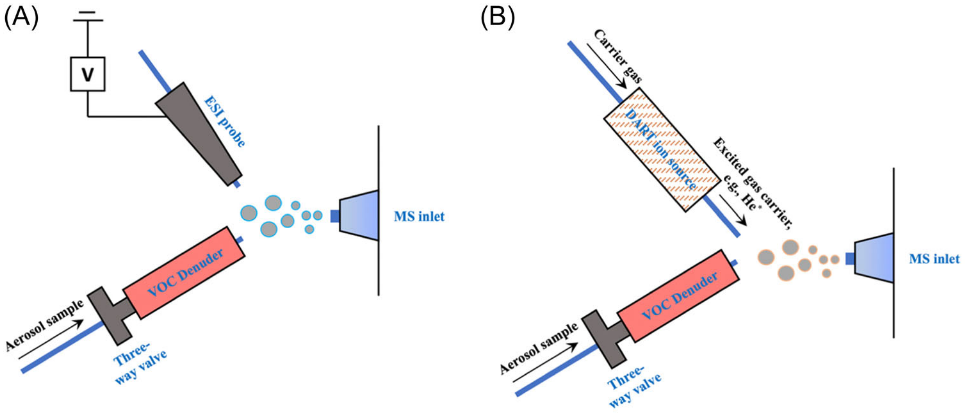

FIGURE 7 Schematics of (A) EESI and (B) DART ion sources interfacing with mass spectrometry. DART, direct analysis in real-time; EESI, extractive electrospray ionization. [Color figure can be viewed at wileyonlinelibrary.com]

inorganic particles during the formation and aging of SOA, meanwhile proving a near molecular-level measurement with high resolution (Gallimore et al., 2017). Furthermore, EESI could combine high time resolution, high resolving power, and detailed structural analysis to provide in-depth understanding of atmospheric chemistry. For instance, Lee et al. have developed an EESI inlet coupled to an Orbitrap to acquire molecular composition of the aerosol components at atmospherically relevant concentrations with ultrahigh mass accuracy and resolution, meanwhile shown the instrument's ability to perform online tandem mass spectrometry analysis (Lee et al., 2020).

Electrospray chemical ionization mass spectrometry (ESCI-MS)

Zhao et al. recently presented a new in-situ ESCI-MS technique by coupling an ESI source to a time-of-flight mass spectrometer (TOF-MS), for the detection of atmospheric inorganic and organic species in the gas phase (Zhao, Chan, et al., 2017). The electrospray is achieved by generating spray droplets via a high-voltage power supply. The salt solutions dissolved in methanol are emitted through a fused silica spray needle housed in a cylindrical evaporation tube and are carried out by a flow of ultrahigh-purity N_2 gas to the IMR, followed by a stainless-steel capillary tube which act as atmospheric pressure interface between the IMR and the mass spectrometer. Any unevaporated droplets are moved out of the effective ionization region by reagent ion source flow, excluding the interference of secondary or extractive ESI. Thus, the sample molecule reacts with the reagent ion to form an ion-molecule adduct via ligand-switching reactions under atmospheric pressure in the IMR. This ESCI technique provides an extended option for both ESI-MS and CIMS applications in measurements of a broad range of atmospheric compounds. Using I^- as the ESCI reagent ion under atmospheric pressure ionization showed high sensitivity for $RO_2^{\bullet}$, allowing for probing specific $RO_2^{\bullet}$ chemistry (Zhao, Thornton, et al., 2018).

PS ionization mass spectrometry (PS-MS)

The PS-MS is a variant of ESI-MS, allowing for direct and indirect detection of dissolved compounds on aerosol filter samples under ambient temperature and pressure (Rindelaub et al., 2016). It has been regarded as a promising offline technique to provide quick and effective filter sample analysis with quantitative capabilities in ambient measurements (Chiang et al., 2018). The paper substrate is soaked or continuously saturated with apposite solvent matrix to generate an electrospray plume from the paper tip under a certain high voltage (Espy et al., 2012; Rindelaub et al., 2016). The typical PS-MS analysis requires no sample preparation, where samples are directly deposited onto the substrate and analyzed by a mass spectrometer (Chiang et al., 2018). Recently, PS-MS has also been used in single droplet analysis, where the filter chromatography papers are cut into triangular piece and then attached to a high-voltage power supply (Kohli & Davies, 2021; Willis et al., 2020). Microdroplets are allowed to fall on the paper. During the formation and transportation process of the spray plume, the analytes in the microdroplets are ionized and transmitted towards the mass spectrometer inlet. Because deposition location of analyte droplets on the paper substrate impact the instrument performance, the spray tip angle and substrate geometry are adjusted to obtain the reproducibility and time scale (Kohli & Davies, 2020, 2021; Willis et al., 2020).

2.2.2 | Other ambient ionization techniques

DART-MS

Among the non-ESI-based ambient ionization mass spectrometry for real-time aerosol characterization, DART is a plasma-based technique that excites ambient molecules into ions through corona discharge of a carrier gas, such as helium, argon or nitrogen (Feider et al., 2019; Zhao, Fairhurst, et al., 2017). Among them, helium is one of the most frequently adopted carrier gas because its electronically excited 2^3S state has 19.8eV of energy capable of ionizing atmospheric molecules (Ai et al., 2018). The excited gas carrier containing metastable atoms flow out of the source to thermally volatilize and ionize analyte molecules which are directly introduced into the ionization region between the DART ion source and the mass spectrometer inlet (Figure 7B) (Feider et al., 2019; Nah et al., 2013). The heated gas can improve the instrument sensitivity by increasing the surface desorption of analyte samples (Wingen & Finlayson-Pitts, 2019). The metastable carrier gas atoms can react with atmospheric water and oxygen molecules to produce a secondary ionizing species such as protonated water clusters (H_3O^+) and molecular oxygen ions (O_2^+) which could ionize sample molecules to form $[M+H]^+$ in the positive mode, and superoxide anions (O_2^-) which incite analytes to $[M-H]^-$ and M^- ions in the negative ion mode through ion-molecule reactions (Cody et al., 2005; Nah et al., 2013; Zhou et al., 2016). Analytes with low ionization energy could be ionized directly during the process (Lam, Kwong, et al., 2019). In recent years, DART-MS has been commonly used to measure aerosol components in multiphase chemistry, such as studying the uptake of gaseous hypochlorous acids (Schwartz-Narbonne et al., 2019), $OH^\bullet$ (Davies & Wilson, 2015; Kwong, Chim, et al., 2018; Lam, Kwong, et al., 2019), and O_3 (Zhou et al., 2016; Zhou, Joudan, et al., 2019; Zhou, Zhou, et al., 2019) on aerosol particles, contributing to the understand of the reaction kinetics and chemical mechanisms of OA aging.

Aerosol flowing ambient-pressure afterglow (AeroFAPA)-MS

The AeroFAPA is another plasma-based soft ambient ionization mass spectrometry used in atmospheric research for real-time characterizing the molecular composition of complex aerosol matrices (Brüggemann et al., 2015, 2017; Fandino et al., 2020; Shelley et al., 2011). This source is based on a helium glow discharge plasma to excite and ionize helium species as the primary reagent ions (Brüggemann et al., 2015). The helium discharge gas can directly desorb and ionize a large range of OA compounds at atmospheric pressure within its high-energy metastable state for mass spectrometry detection in the afterglow region. The particle-phase analytes need to have a certain volatility to be ionized during the temperature-driven desorption process. Besides, the usage of helium source allows for longer lifetime of the ion source electrodes due to its low sputtering activity. Similar to the DART source, the AeroFAPA technique utilizes ambient O_2 and H_2O to produce O_2^- ions through the interaction of thermal electrons and subsequently ionize aerosol molecules to form negatively charged analyte ions (Aghaei & Bogaerts, 2021). In addition to O_2^- ions, the signals of other reagent ions, like O^-, OH^-, HO_2^-, O_3^-, NO_2^-, and NO_3^- ions are observed in the negative mode (Schilling et al., 2010; Shelley et al., 2011). On the other hand, in the positive-mode measurements, the presence of O_2^+, N_2^+, NO^+, O_2^+, NO_2^+ as well as protonated water clusters has been reported, and these reagent ions are produced via the charge-transfer reactions between the AeroFAPA source with N_2 and H_2O molecules in the air (Schilling et al., 2010).

Ambient ionization without external energy

A few ambient ionization methods were recently employed to study OA composition that do not require external energy such as high voltage or heating. Sonic-spray ionization (SSI) is one of these methods (Hirabayashi et al., 1994; 1995; Wingen & Finlayson-Pitts, 2019). In SSI, the mechanical action of sheath gas flow approaches sonic velocities and generates excess charges on aerosol particles and droplets, leading to gas-phase ions. In a recent study by Wingen and Finlayson-Pitts, this method was applied to solid particles with core-shell morphologies (Wingen et al., 2019a). SSI turned out to be surface-sensitive and was used to probe the surface composition of laboratory OA. Similar to SSI, droplet-assisted ionization (DAI) as an inlet ionization technique has been recently developed for online aerosol characterization, with the advantage of no need for sample preparation or high voltage utilization (Kerecman et al., 2021). The inlet interface consists of a temperature-controlled stainless-steel capillary tube. The analyte-doped droplets within water matrix are charged when they pass through the capillary from atmospheric pressure into a vacuum, and then gas-phase molecular ions are produced after these droplets undergo aerodynamic and/or thermal breakup due to pressure and temperature gradients (Apsokardu et al., 2020, 2021; Horan et al., 2017; Kerecman et al., 2021). DAI-MS has been applied in characterization of airborne nanoparticles (Horan et al., 2017) and the molecular components of α-pinene SOA including HOM monomers and dimers with oxygen atom number as high as 14 (Kerecman et al., 2021). Another soft ambient ionization method without coupling to an external ionization source named inlet or vacuum ionization has been developed to study aerosol surface composition (Pagnotti et al., 2011). In a recent work reported by Qin et al., a triple quadrupole mass spectrometer is used to monitor aerosol interfacial molecular composition without an ion source (Qin et al., 2022). Instead, the sublimation of solid core materials (e.g., glutaric acid) in the particles leads to the ejection of molecular ions of the surface compounds. By comparing the mass spectral intensities of core and surface materials under different coating thicknesses, the proposed ionization scheme was verified. These surface-sensitive approaches were also found to have minimal decomposition of the analyte, providing new paths for understanding the surface composition of atmospheric aerosols.

2.3 | Novel coupling of separation techniques and mass spectrometry

Despite that the greatly improved mass spectrometry techniques for atmospheric chemistry in the past few years have enabled lower detection limits, higher mass and time resolutions, and more comprehensiveness, structure identification, and isomer separation are still challenging for mass spectrometry by itself. Tandem mass spectrometry is useful to study chemical structures for targeted analysis, but to resolve the structural/isomeric information of complex and unknown atmospheric species in a nontargeted fashion, mass spectrometry needs to be coupled with separation techniques. Column-polarity-based methods (e.g., GC and LC) are well-established separation techniques to characterize atmospheric species on the isomer-resolved level. In addition, ion mobility spectrometry (IMS) separation coupling to mass spectrometry has been recently shown as a promising approach in aerosol research. In this section, we review new advances in GC, LC, and IMS coupled to mass spectrometry.

2.3.1 | GC-CIMS

GC can separate and quantitatively characterize chemical components in complex mixtures with structural information. However, previous GC analysis usually requires sample collection and preconditioning steps, and the separation effectiveness for certain chemical classes largely relies upon the column selection (Bi et al., 2021b). The traditional GC-MS uses either the hard EI ionization, or the relatively softer chemical ionization with reagents such as methane (Jaoui et al., 2005, 2008; Yu et al., 1998). In the past several years, the development of CIMS with a variety of ionization methods led to the emergence of coupling GC and CIMS in new fashions, to provide near real-time isomer identification and quantification.

In the recently developed real-time GC-CIMS by the Wennberg group at Caltech which focused on polar oxygenated VOCs (Bates et al., 2014; Teng et al., 2015, 2017; Vasquez et al., 2018; Xu et al., 2019; Xu, Møller, et al., 2020), the sampling gases are firstly collected on the head of an RTX 1701 GC column cooled to a desired temperature using an isopropanol bath or liquid CO_2. Then analytes elute in an order depending on their polarity and are separated by the retention time. The GC eluates are diluted by carrier N_2 gas and transmitted to the IMR region of CIMS that uses CF_3O^- as the reagent ion (see Section 2.1.2). The GC-CF_3O^--CIMS can determine important atmospheric isomeric components, such as isoprene epoxydiols (IEPOX) (Bates et al., 2014) and organonitrates (Kurtén et al., 2017; Praske et al., 2018; Teng et al., 2015; Vasquez et al., 2018).

Recently, Bi et al. coupled a thermal desorption aerosol gas chromatograph (TAG) to CIMS to expand GC-CIMS capability to also measure particle-phase compounds (Bi et al., 2021a). The TAG is a custom-built instrument including a sampling cell, an automatic liquid injection system, and preseparation process of a polar GC column (Isaacman et al., 2014; Williams et al., 2006; Zhao et al., 2013). In TAG-CIMS, aerosol samples are collected by the sampling cell while chemical standards are injected into the cell automatically by a liquid injection program. These compounds are thermally desorbed in helium to the column head and are separated by passing through the GC column. Moreover, the analytes may be derivatized to improve transmission efficiency and stability for the analysis of oxygenated organic compounds (Isaacman-VanWertz et al., 2016). By coupling a TAG to a CIMS, the mass resolution of individual molecules is enhanced at the cost of extended analysis time. Bi et al. further developed a multi-reagent ionization mode for TAG-CIMS in which I^- and zero air are both used as reagent gases (Bi et al., 2021a). This mode could determine additional chemical species by the high abundance of non-adduct ions without losing the original advantage to use I^- clusters to identify oxygenated compounds.

2.3.2 | New methods based on LC-MS

Similar to GC-MS, LC-MS is another well-established analytical chemistry technique to combine the separation of dissolved aerosol mixtures by LC and the mass analysis capabilities of molecularly resolved information provided by mass spectrometry. A LC-MS system equipped with an ESI and/or an atmospheric pressure chemical ionization (APCI) source is extensively used for molecular-level characterization and analysis of polar or water-soluble organic molecules commonly found in complex samples of atmospheric aerosols (Brecht et al., 2020; Dye & Yttri, 2005; Souverain et al., 2004; Surratt et al., 2006; Surratt, Kroll, et al., 2007; Surratt, Lewandowski, et al., 2007; Szmigielski et al., 2007; Zhang, Dalleska, et al., 2016).

Iodometry-assisted LC-MS

Organic peroxides have been shown to account for a major fraction of SOA (Bateman et al., 2011; Docherty et al., 2005; Epstein et al., 2014; Li et al., 2016; Mertes et al., 2012; Yao et al., 2019). In traditional studies, quantification of organic peroxides was achieved by using spectroscopic techniques coupled with iodometry. However, this method only determines total organic peroxide molar mass. Molecular characterization cannot be achieved using this approach, hindering the understanding of the organic peroxide composition. Recently, Zhao et al. combined the iodometry with LC-ESI-MS and showed that by comparing the peaks in the LC-ESI-MS with and without the iodometry treatment, specific organic peroxide species in SOA can be identified with molecular and sometimes structural information (Zhao, Kenseth, Huang, Dalleska, Kuang, et al., 2018; Zhao, Kenseth, Huang, Dalleska, & Seinfeld, 2018). In this approach, the collected SOA samples on filters are first extracted using traditional methods (Surratt et al., 2006; Zhang et al., 2011). The extract solutions are subsequently divided into two aliquots of which one is treated with iodometry and the other without, and the concentration of a peroxide compound is achieved by comparing the signals of ions with the same retention time according to the base peak intensity chromatograms. The iodometry-assisted LC-ESI-MS were furthered used for isomer-level identification and characterization of organic peroxides from monoterpene SOA (Wang et al., 2021; Yao et al., 2022; Zhao, Yao, et al., 2022), as well as for kinetics and chemical aging of isomer-resolved peroxide hydrolysis in aqueous-phase (Liu et al., 2022).

LC-MS with HILIC column

Another recent development of LC techniques is to use a hydrophilic interaction liquid chromatography (HILIC) to study polar hydrophilic species in aerosol chemistry. Traditionally, reverse-phase liquid chromatography (RPLC) has been a popular method to detect polar and water-soluble components. However, RPLC measurements are extremely limited by its performance in short retention times, ion suppression effects or poor peak shapes. It has been proved that HILIC could effectively separate water-soluble organosulfates, showing its potential to identify and quantify isoprene SOA constituents (Hettiyadura et al., 2015, 2017; Spolnik et al., 2018). In the study by Cui et al., an ultra-performance liquid chromatography (UPLC) with a HILIC column is interfaced to ESI-MS to measure water-soluble IEPOX-derived SOA isomers in the negative mode (Cui et al., 2018). The UPLC parameters, such as buffers, pH values, and column temperatures, can be optimized to increase the sensitivity. The mobile phases are composed of eluents containing ammonium acetate and water, sometimes ACN, of which the eluent pH is adjusted to 9.0 with NH_4OH buffer. The column is held at a constant heated temperature (~35°C). The relatively low temperature used in the HILIC method reduces the decomposition of organosulfates and other IEPOX-derived components, improving its ability to distinguish water-soluble isomers and evaluate SOA yields in isoprene-rich regions.

2.3.3 | IMS-MS

IMS as a powerful analytical technique has gained attention and prominence for separating structural isomers that have different molecular shapes over the last 20 years (Ewing et al., 2001; Kanu et al., 2008). But only very recently, this technique started to be applied in the field of atmospheric chemistry to separate and detect both gas- and particle-phase atmospheric constituents on the isomeric level (Krechmer et al., 2016; Mayorga et al., 2021; West et al., 2023; Zhang, Krechmer, et al., 2016; Zhao, Mayorga, et al., 2020; Zhao et al., 2021). In the drift-tube-based IMS, ionized molecules can be separated based on their ion mobilities which arises from their collisional cross sections (CCS) and ion-molecule interactions in an inert carrier buffer gas (e.g., He or N_2). An ionization source (usually ESI and APCI) can generate charged analytes of interest under controlled pressure and temperature, and the ions are then separated in the IMS drift tube (Mayorga et al., 2021; Valadbeigi et al., 2019; Valadbeigi, Azizmohammadi, et al., 2020; Valadbeigi, Ilbeigi, et al., 2020; Zhao, Tolentino, et al., 2019; Zhao, Mayorga, et al., 2020; Zhao et al., 2021; Zheng et al., 2018). The IMS drift tube is followed by a pressure reduction interface, after which ions are transmitted into the mass analyzer (Kanu et al., 2008).

The recently developed IMS-MS by Tofwerk Inc. and Aerodyne Research Inc. uses the TOF mass analyzer, similar to their TOF-CIMS configuration (see Section 2.1). Between the IMS and the TOF, the potential differences between the two quadrupoles are used for collision-induced dissociation (CID) analysis where molecular ions are fragmented and weakly bound ion clusters are dissociated (Kaplan et al., 2010). The resultant fragmentation mass spectrum is similar to traditional tandem mass spectrometry measurements but providing additional information of relationships between precursor ions and fragment ions as well as spectra over the entire mass-to-charge range (Krechmer et al., 2016). IMS-MS measurements are not constrained by solvent or stationary-phase like traditional LC or GC, but still allow for the ability to distinguish organic species with different structures. The drift times are instrumental-dependent value which are transferable under the same buffer gas and temperature conditions, so that the measured CCS therefore are comparable to provide structural information (Krechmer et al., 2016).

Another recent application of IMS-MS was used in the real-time analysis of aerosol particles in prebiotic chemistry with a vacuum-assisted plasma ionization (VaPI) source to ionize organic molecules (Blair et al., 2018). The VaPI ion source utilizes a glow discharge at near atmospheric pressure to generate heated plasma gases. The aerosols sampled by a sampling tee collide with the plasma gas to be chemically ionized through proton transfer reactions. Then ions of interest are transferred from the sampling tee to an IMS-MS instrument for real-time analysis. Besides, the signals of oligomer clusters formed from ion-molecule reactions are observed in real-time, indicating the high reactivity of the

VaPI source to provide new insights into the prebiotic aerosol chemistry.

3 | APPLICATIONS OF THE NEW MASS SPECTROMETRY TECHNIQUES IN ATMOSPHERIC CHEMISTRY RESEARCH

The advances in mass spectrometry techniques described above are crucial for understanding the molecular and even isomeric compositions of complex atmospheric components in both the gas and particle phases and help elucidate the processes that lead to the formation and evolution of atmospheric organic species (Ehn et al., 2014; Kroll & Seinfeld, 2008; Smith et al., 2009). In the forthcoming section, we summarize the recent applications of these techniques to highlight the key progress in the characterization and identification of a broad range of organic species in atmospheric chemistry.

3.1 | Detection of atmospheric VOCs from traditional and emerging sources

VOCs are ubiquitous in the Earth's atmosphere. Speciation and quantification of VOCs are thus critical for understanding their emission sources, oxidation chemistry, and impacts on air quality and climate. PTR-MS is a key technique to quantitatively and sensitively measure a large variety of VOCs in real-time. The design and performance of PTR-MS have been extensively reviewed in previous publications (de Gouw & Warneke, 2007; Yuan et al., 2017). The sensitivities to different VOCs increase linearly as a function of the proton-transfer reaction rate, illustrating the quantitative ability of PTR-MS to atmospheric gas tracers (Krechmer et al., 2018; Sekimoto et al., 2017). Yet, some VOCs under ambient conditions may have very low concentrations (e.g., pptv or even sub-pptv levels), for which detection and quantification are still challenging. In this section, we will mainly focus on specific applications of the new versions of PTR-MS, namely Vocus and PTR3, in laboratory investigation and field work of atmospheric organic vapors and show their comparison with conventional PTR-MS.

With the greatly improved sensitivity and resolving power, the Vocus PTR-TOF allows for better quantification for VOCs with high molecular weight (e.g., *m/z* 150–300 Th) than traditional PTR-TOF (Figure 4) (Riva, Rantala, et al., 2019). It has been recently used to characterize and quantify VOCs and their oxidation products in both laboratory studies and field measurements (Koss et al., 2020; Krechmer et al., 2018; Li et al., 2021; Sumlin et al., 2021; Wang, Mehra, et al., 2020; Wu et al., 2021; Zaytsev, Koss, et al., 2019). For example, in the first study of VOCs in forested regions using Vocus PTR-TOF, abundant terpene-derived VOCs consisting of comprehensive elemental composition classes with CH, CHO, CHN, CHS, CHON, CHOS were reported, while oxygenated products with carbon numbers of 5–10, 15, and 20 are dominant among the hydrocarbon categories (Li et al., 2020). The low-volatility diterpenes was observed in real-time in ambient air for first time using Vocus PTR-TOF at 2 ppt level. Vocus PTR-TOF can also efficiently detect the less oxidized organic nitrates and other nitrogen-containing organic compounds (DeVault & Ziemann, 2021), such as the product of alkyl nitrite photolysis (Nihill et al., 2021) and the organic nitrates from aromatic VOCs oxidation under varied NO_x conditions (Mehra et al., 2020). Besides the detection of atmospheric VOCs from traditional biogenic and anthropogenic sources, Vocus PTR-TOF has also shown promising capability to study VOCs from emerging sources such as the volatile chemical products (VCP) and wildfires (Jensen et al., 2021; Liang et al., 2022; Majluf et al., 2022). In addition, Vocus PTR-TOF has allowed for the quantitative source attribution of indoor VOC emissions (Liu & Abbatt, 2021; Pagonis, Price, et al., 2019). For instance, it is applied in the detection and quantification of numerous products from human skin ozonolysis (Morrison et al., 2021), the quantitative analysis of metabolic exhaled breath (Bruderer et al., 2019), the dark production of potentially toxic cyanogen chloride during blench cleaning process (Mattila et al., 2020), and the examination of VOCs and crystal monomers released from liquid crystal display screens (Liu & Abbatt, 2021).

Very similar to Vocus PTR-TOF, PTR3 is well suited to detect atmospheric VOCs due to its high sensitivity to atmospheric trace gases, resulting in one of its widest usages to monitor the gas-phase reactant precursors in the new particle formation (NPF) studies. For example, PTR3 has been used in NPF studies through monitoring the gas-phase reactant concentrations of isoprene (Caudillo et al., 2021; Heinritzi et al., 2020), monoterpenes (Caudillo et al., 2021; Lehtipalo et al., 2018; Pullinen et al., 2020; Wagner et al., 2017; Yan et al., 2020) and other VOCs (Koss et al., 2020; Lehtipalo et al., 2018; Stolzenburg et al., 2020; Wang, Kong, et al., 2020). In α-pinene ozonolysis experiments conducted in the CLOUD chamber, PTR3 shows good agreement of oxidation products with a NO_3^--TOF-CIMS (Bianchi et al., 2019; Breitenlechner et al., 2017). In this study, over 1000 formulas were obtained by PTR3, showing a detection range for broader volatility compound species with much higher sensitivity to α-pinene and monomeric and dimeric oxidation products (Figure 8) (Breitenlechner et al., 2017). Further, as mentioned above, Zaytsev et al. developed a novel instrumentation based on PTR3 with switching regent ions of H_3O^+ and NH_4^+ for qualitative and quantitative measurements of VOCs with a large range of volatilities (Zaytsev, Breitenlechner, et al., 2019). This technique was used to detect and quantify both ring-retaining products and ring-scission products derived from a series of toluene and 1,2,4-trimethylbenzene photooxidation, while the H_3O^+ mode is more sensitive to less oxidized molecules but NH_4^+ to larger and more functionalized compounds (Zaytsev, Koss, et al., 2019).

3.2 | Highly oxidized molecules (HOMs)

The HOMs are a class of organic compounds containing six or more oxygen atoms with high O/C ratios, usually formed via autoxidation chemistry involving $RO_2^\bullet$ in the atmosphere (Bianchi et al., 2019; Ehn et al., 2014; Krechmer et al., 2015). They consist of a wide range of chemical functional groups (e.g. −OH, =O, and −OOH) and may be key components of atmospheric SOA after partitioning to the particle phase due to their extremely low volatility (Berndt, Richters, et al., 2016; Crounse et al., 2013; Jokinen et al., 2015). In this section, we will review recent studies that applied the above-described mass spectrometry techniques to characterize and quantify HOMs.

Because HOMs are formed from $RO_2^\bullet$ autoxidation, it is thus important to detect not only the closed-shell HOMs themselves but also the HOMs-$RO_2^\bullet$. This was shown to be feasible by using CIMS with NO_3^-, $CH_3C(O)O^-$, I^-, Br^-, NH_4^+, and pronated amines as the reagent ions (see Table 1) (Berndt, Herrmann, et al., 2016; Berndt et al., 2017; Berndt, Scholz, et al., 2018; Hansel et al., 2018; Priestley et al., 2021; Wang, Kong, et al., 2020; Zaytsev, Koss, et al., 2019; Ehn et al., 2014). Among these methods, NO_3^--CIMS has the highest selectivity to HOMs with high number of oxygens and was the first technique developed for HOMs detection (Berndt, Richters, et al., 2016; Ehn et al., 2014; Jokinen et al., 2015; Richters et al., 2016). It observed HOMs formation from oxidation of monoterpenes (Ehn et al., 2012; Ehn et al., 2014; Jokinen et al., 2015; Rissanen et al., 2019), isoprene (Jokinen et al., 2015; Massoli et al., 2018), aromatic VOCs (Guo, Yan, et al., 2022; Molteni et al., 2018; Priestley et al., 2021), and other VOCs (Bianchi et al., 2016; Richters et al., 2016; Rissanen et al., 2019). Initial studies using NO_3^--CIMS, concluded that HOMs are formed at higher yields in monoterpene ozonolysis, but not in $^\bullet$OH oxidation (Ehn et al., 2014). However, later studies by Berndt et al. found that $^\bullet$OH oxidation of monoterpenes also produces high yields of HOMs, which can be more sensitively detected by $CH_3C(O)O^-$-CIMS (Berndt, Richters, et al., 2016). This results also suggest that CIMS with different ionization methods may lead to distinct sensitivities for different HOMs molecules. In addition, Br^- and I^- are the other two reagent ions to couple with CIMS and measure HOMs (Mohr et al., 2017; Priestley et al., 2021; Wang, Kong, et al., 2020; Zhao, Thornton, et al., 2018; Zhao et al., 2021). They are less selective than NO_3^- and $CH_3C(O)O^-$. Further, NH_4^+-CIMS is the least selective method among the mentioned ion chemistries which measures a wide range of species from hydrocarbons to HOMs (Hansel et al., 2018). Consistently, the new NH_4^+ PTR3 has been

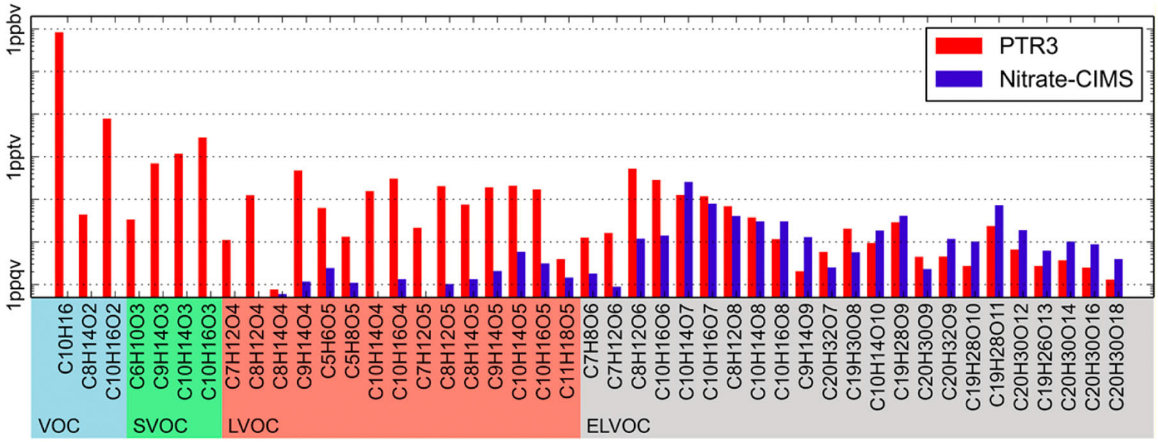

FIGURE 8 PTR3 (red) and NO_3^--TOF-CIMS (blue) results from an ozonolysis experiment of 1 ppb α-pinene and 40 ppb ozone at the CLOUD chamber at 5°C and a relative humidity of 38%. Exact masses were used to assign sum formulas that are organized as a function of saturation vapor pressure ranging by volatilities. Reproduced with permission Breitenlechner et al. (2017). Copyright 2017 American Chemical Society. [Color figure can be viewed at wileyonlinelibrary.com]

shown to be more sensitive to HOMs with low volatility in the atmosphere than a typical PTR-TOF (Breitenlechner et al., 2017). Lastly, protonated amines as the reagent ions have been used to measure HOM dimer formation from $RO_2^\bullet$ cross-reactions in the oxidation of α-pinene (Berndt, Mentler, et al., 2018) and 1,3,5-trimethylbenzene (Berndt, Scholz, et al., 2018).

In addition to CIMS, Zhao et al. applied different reagent ions (e.g., I^-, NO_3^-, $C_2H_3O^-$, Li^+, Na^+, K^+, and NH_4^+) to the ESCI-MS, and compared the obtained gas-phase chemical composition including HOMs from α-pinene ozonolysis with typical CIMS (Zhao, Chan, et al., 2017). They concluded that ESCI-MS with I^- as reagent ions have high sensitivity, comparable to the I^--CIMS. It was also found that monomeric products ($n_C \leq 10$) are evident in all ion modes, but most dimeric products are only observed in the Na^+ ion mode. Besides, the reagent ion Na^+ is more sensitive to less oxidized species ($n_O \leq 3$) than I^- or NO_3^-, consistent with the observations in previous studies (Hyttinen et al., 2015; Iyer et al., 2016; Lee et al., 2014). CIMS with both I^- and NO_3^- could detect HOMs with similar oxygen contents, while the different signal intensities might be caused by the identities and locations of the functional groups (Berndt, Richters, et al., 2016; Lee et al., 2014). In a later study, Zhao et al. used I^--ESCI-MS coupled with a LTOF device to detect HOMs derived from α-pinene ozonolysis, including 150 gaseous dimers identified as $C_{16-20}H_{24-34}O_{4-13}$ which contribute to 5%–60% of SOA mass yields (Zhao, Thornton, et al., 2018).

Besides the measurements of gaseous HOMs using CIMS with the above-mentioned reagent ions, CIMS can be coupled with a FIGAERO to detect the condensed HOMs in the particle phase (Lopez-Hilfiker et al., 2015; Mohr et al., 2017; Mutzel et al., 2015; Zhang et al., 2015). For example, Mohr et al. reported an ambient observation in Finland that a large variety of dimers with $C_{16-20}H_yO_{6-9}$ were formed from monoterpene oxidation in both the gas and particle phases by employing $CH_3C(O)O^-$ and I^- as the reagent ions in FIGAERO-CIMS (Mohr et al., 2017). In this study, the total dimer concentrations were quantified in the two phases on the same order of magnitude and estimated a dimer contribution of 5% to the early stage of particle growth, highlighting the importance of HOMs condensation for aerosol growth. In addition to the FIGAERO-CIMS measurements, ESI-based techniques have also been used to monitor HOMs in the particle phase, both in real-time and offline. Specifically, EESI-MS has been used to characterize HOMs in SOA from α-pinene ozonolysis as well as the real-time degradation of individual monomer and dimer HOMs species to investigate the effect of HOMs on the SOA evolution (Figure 9) (Pospisilova et al., 2021). Through the online EESI-MS characterization of SOA composition, this study further proposed that particle-phase reactions such as the decomposition of reactive oxygen species and the evaporation of volatile carboxylic acid play an important role in the SOA aging (Pospisilova et al., 2020). Lee et al. used EESI-MS to measure the monomer and dimer HOM distributions in α-pinene SOA, which showed good agreement with other particle-phase HOMs measurements using offline techniques (Bianchi et al., 2019; Kerecman et al., 2021; Lee et al., 2020). Furthermore, in a Zurich field deployment of EESI-MS, a similar result of dominant factors and mechanisms in the oxidation of monoterpenes has been reported to be consistent with NO_3^--CIMS measurements of gas-phase HOM formation in a Finland forest (Stefenelli et al., 2019; Yan et al., 2016). Finally, organic nitrate HOMs were observed in the $NO_3^\bullet$-derived α-pinene SOA using both FIGAERO-CIMS and EESI-MS, suggesting their large contribution to SOA aging (Bell et al., 2022; Guo, Shen, et al., 2022).

Other than the CIMS and EESI applications, recent developments in the combination of separation methods with mass spectrometry have also enabled new findings on HOM formation and composition. Krechmer et al. employed IMS-MS with the NO_3^- chemical ionization source for online measurements of gas-phase HOMs derived from α-pinene and limonene oxidation, meanwhile the number of isomers for each HOM formula is obtained by drift times (Krechmer et al., 2016). Zhang et al. present the characterization of α-pinene derived HOMs in the form of $C_{8-10}H_{12-18}O_{4-9}$ monomers and $C_{16-20}H_{24-36}O_{8-14}$ dimers using IMS-MS with ESI (Zhang et al., 2017). In this work, through the application of CID to fragment dimer ions after mobility separation, the fragmented monomer ions with the same drift time can be determined; hence, IMS-MS enables the investigation of HOM dimer structures (Figure 10). Zhao et al. coupled IMS-MS with I^--CIMS analysis to separate and identify isomeric HOMs from α-pinene ozonolysis, and proposed an autoxidation rate of 20-fold faster of ring-opened $C_{10}H_{15}O_4$ $RO_2^\bullet$ than the ring-retained ones which are produced simultaneously in α-pinene ozonolysis (Zhao et al., 2021). Integrating IMS-MS and I^--CIMS measurements, Mayorga et al. observed a series of HOMs characterized as organic nitrates and nitrooxy $RO_2^\bullet$ derived from the oxidation of limonene, meanwhile emphasized a significant contribution of nitrooxy $RO_2^\bullet$ autoxidation and sequential $NO_3^\bullet$ oxidation to HOM yields (Mayorga et al., 2022). Moreover, the iodometry-assisted LC-ESI-MS method was used to study the fate of peroxide monomers ($C_{8-10}H_{12-18}O_{5-8}$) and dimers ($C_{15-20}H_{22-34}O_{5-14}$) in SOA samples derived from α-pinene oxidation, demonstrating the potential of

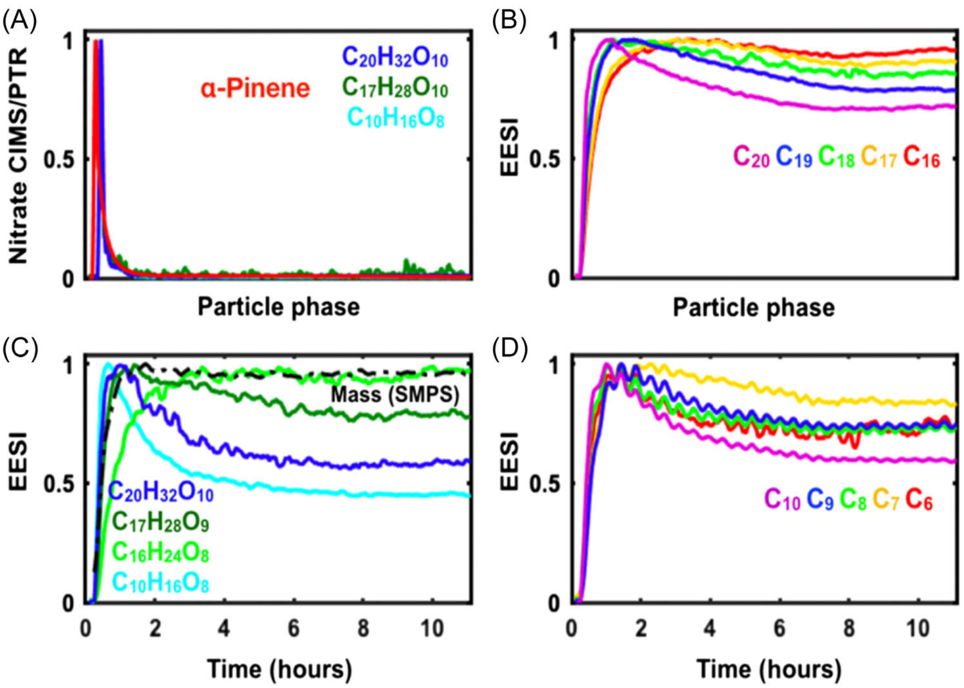

FIGURE 9 Time evolution of particle and gas-phase composition for α-pinene ozonolysis. (A) α-Pinene injection into the chamber (~35 ppbv) measured by PTR-TOF and gas-phase evolution of its oxidation products measured by NO_3^--TOF-CIMS. (B) Time evolution of particle phase dimers, grouped by their carbon number. (C) Time evolution of three dimers and one monomer measured in the particle phase showing very distinct behavior despite similar saturation vapor concentration. (D) Time evolution of particle phase monomers, grouped by their carbon number. All signals are normalized to the maximum EESI-MS signal recorded for the respective ion during the displayed period. Reproduced with permission Pospisilova et al. (2020). Copyright 2020 Pospisilova et al. CIMS, chemical ionization mass spectrometer; EESI-MS, extractive electrospray ionization-mass spectrometry; PTR-TOF, proton transfer reaction-time-of-flight. [Color figure can be viewed at wileyonlinelibrary.com]

iodometry-assisted LC-ESI-MS to separate and identify HOMs that contain peroxide functional groups on the isomeric level (Figure 11) (Yao et al., 2022).

3.3 | Real-time OA bulk and surface molecular composition

Real-time measurements of OA molecular composition have long been desired. Although thermal desorption methods coupled with CIMS have made this possible (Lopez-Hilfiker et al., 2014; Thornton et al., 2020; Zhao, Xu, et al., 2019), heating-induced artifacts have been a concern to interfere accurate interpretation of OA molecular composition. In contrast, the recently developed EESI-MS overcomes the issue and is able to perform online OA molecular composition without extensive heating (Lopez-Hilfiker et al., 2019; Pagonis et al., 2021; Qi et al., 2019). Despite the ongoing debate of the ionization mechanism by EESI, it is often considered to measure the compositions of the aerosol bulk (Pagonis et al., 2021). In recent EESI-MS studies, the spray solution is usually a mixture of water and methanol/acetonitrile, doped with ~100 ppm of a strong ionic compound like sodium iodide, such that analytes are detected as $[M+Na]^+$ adducts in positive mode and as $[M-H]^-$ ions in the negative mode (Lee et al., 2020; Lopez-Hilfiker et al., 2019; Pagonis et al., 2021). EESI-MS quantification can be accomplished by performing mass calibrations of atomized aerosol particles, where ion abundance displays a linear response to mass due to the lack of matrix interference (Brown et al., 2021; Gallimore et al., 2017; Stefenelli et al., 2019). EESI-MS has been successfully deployed for ground-based ambient sampling, aircraft tests, and laboratory experiments, demonstrating its versatile applications and reliable performance in various environmental conditions (Heald & Kroll, 2020; Hodshire et al., 2019; Lopez-Hilfiker et al., 2019; Pagonis et al., 2021; Pospisilova et al., 2020; Takhar et al., 2021). In an example of EESI-MS performance shown in Figure 12, the time series of levoglucosan and nitrocatechol measured by EESI-MS in wildfire smoke aerosols exhibited excellent agreements with other bulk aerosol measurements and gas-phase tracers (Pagonis et al., 2021).

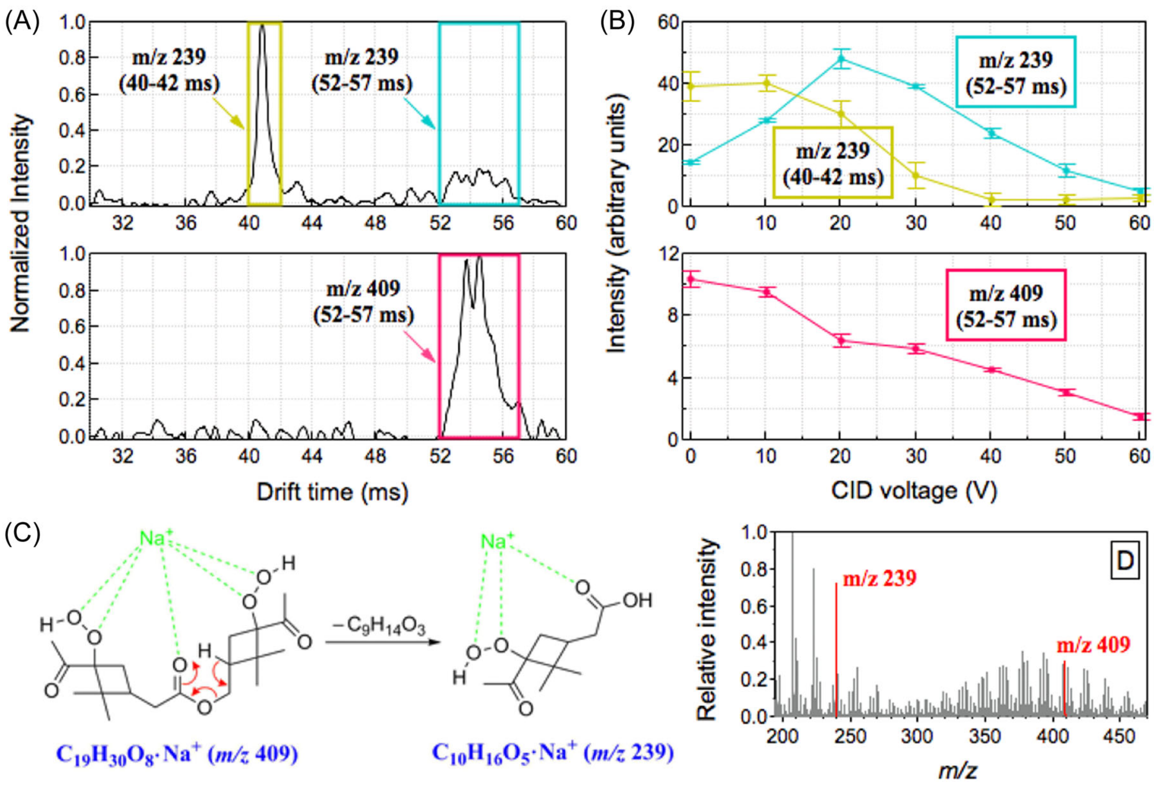

FIGURE 10 (A) Ion mobility spectra for one pair of precursor-fragment ion adducts as a representative example of the dimers from α-pinene ozonolysis. The ion adduct at *m/z* 239 Th with a drift time of 40–42 ms is assigned to a monomer product ($C_{10}H_{16}O_5$) and the ion adduct at *m/z* 409 Th with a drift time of 52–57 ms is assigned to a dimer product ($C_{19}H_{30}O_8$). The ion adduct at *m/z* 239 Th with a drift time of 52–57 ms is assigned to the fragment ion from CID of its precursor ion at *m/z* 409 Th. (B) Intensity profiles of these three ion adducts as a function of the collision energy, as characterized by the CID voltage. (C) Proposed McLafferty rearrangement for the CID of the $C_{19}H_{30}O_8Na^+$ dimer to the $C_{10}H_{16}O_5Na^+$ monomer. (D) Positive IMS-MS mass spectrum of SOA from α-pinene ozonolysis. Reproduced with permission Zhang et al. (2017). Copyright 2017 American Chemical Society. CID, collision-induced dissociation. [Color figure can be viewed at wileyonlinelibrary.com]

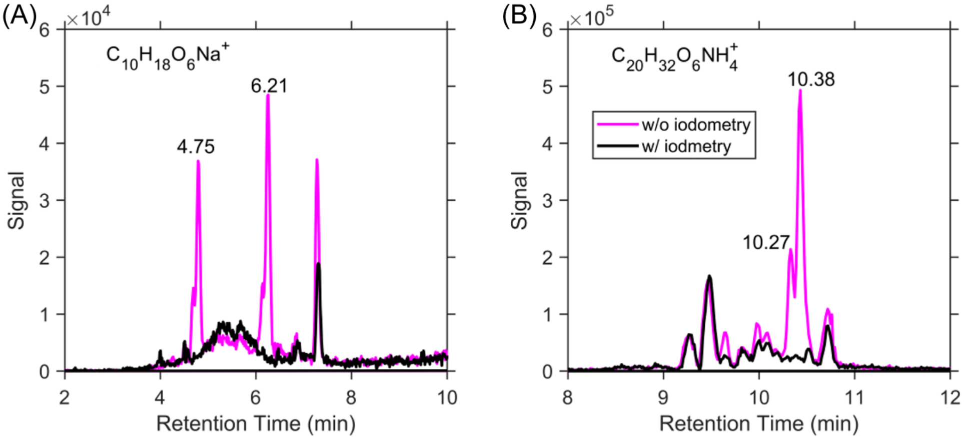

FIGURE 11 Extracted LC-ESI-MS ion chromatograms of (A) $C_{10}H_{18}O_6Na^+$ and (B) $C_{20}H_{32}O_6NH_4^+$ measured for SOA samples treated with (black) and without (magenta) iodometry. The isomer peaks of $C_{10}H_{18}O_6Na^+$ at 4.75 and 6.21 min and $C_{20}H_{32}O_6NH_4^+$ at 10.27 and 10.38 min are assigned to organic peroxides. Reproduced with permission Yao et al. (2022). Copyright 2022 American Chemical Society. LC-ESI-MS, liquid chromatography-electrospray ionization-mass spectrometry. [Color figure can be viewed at wileyonlinelibrary.com]

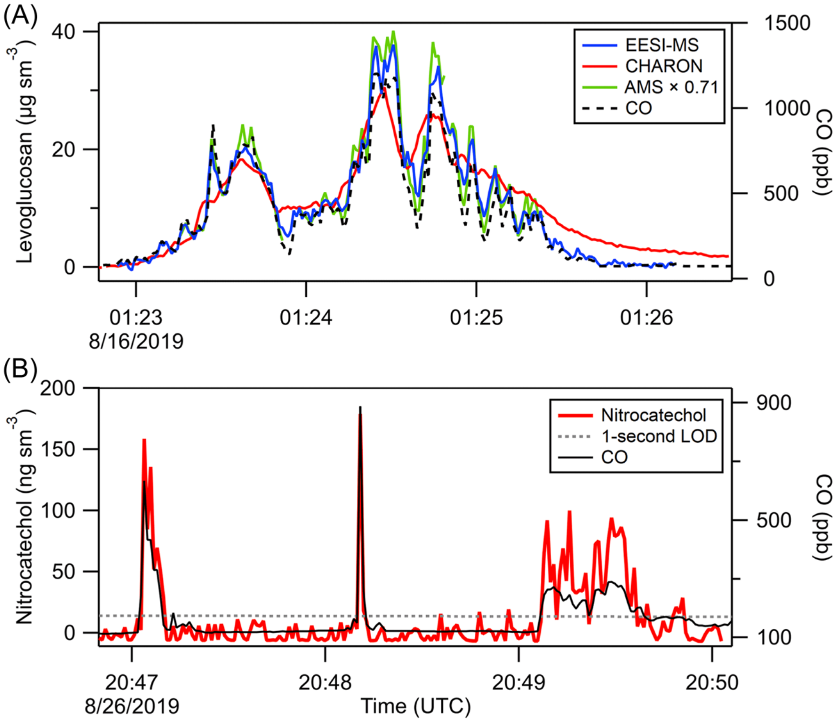

FIGURE 12 Examples of (A) levoglucosan and (B) nitrocatechol time series measured by EESI-MS from wildfire smoke aerosol, including comparison to CHARON PTR-MS and AMS (scaled by a factor of 0.71 to show temporal agreement). Carbon monoxide measurements are included to show the boundaries and structure of the smoke plumes. Reproduced with permission Pagonis et al. (2021). Copyright 2021 Pagonis et al. AMS, aerosol mass spectrometer; EESI-MS, extractive electrospray ionization mass spectrometry; PTR-MS, proton transfer reaction-mass spectrometry. [Color figure can be viewed at wileyonlinelibrary.com]

Qi et al. and Stefenelli et al. presented some of the first ambient measurements using EESI-MS to characterize OA molecular composition in Zurich, a Switzerland urban site (Qi et al., 2019; Stefenelli et al., 2019). In these studies, the real-time analysis for atmospheric aerosols on a near-molecular level was provided to determine the emissions sources and investigate physicochemical processes. Coupling the EESI-MS measurements with positive matrix factorization (PMF) analysis, these studies determined biogenic emissions as major and secondary sources contributing to OA mass during summer and winter, respectively. Furthermore, through combining with colocated measurements, various EESI-MS studies of the ground and aircraft aerosol samples provided valuable insights into the OA bulk properties and molecular composition, suggesting that the unban OA were mostly derived from oxidation of terpenes and aromatic hydrocarbons (Chen et al., 2020; Mehra et al., 2020), biomass burning (Pagonis et al., 2021; Qi et al., 2019, 2020; Yazdani et al., 2021), cigarette smoke (Qi et al., 2019, 2020), and cooking emissions (Takhar et al., 2021). EESI-MS has also been applied in *in-situ* analysis of metals in aerosols. A wide range of ion adducts formed by the reactions between disodium ethylenediamine tetraacetic acid (EDTA) dihydrate and water-soluble metal compounds and trace elements were detected using the negative ion mode (Giannoukos et al., 2020). Moreover, EESI-MS was used in the indoor air studies for quantitative OA composition measurements. Brown et al. have detected over 200 unique indoor OA molecular species using EESI-MS, including fatty acids, carbohydrates, phthalates, and low-volatility siloxanes, which are strongly consistent with the results from FIGAERO-CIMS and other techniques (Brown et al., 2021).

In laboratory studies, researchers have used EESI-MS to measure the molecular composition and time series of oxidation products in α-pinene derived SOA in both positive and negative ion modes (Gallimore et al., 2017; Pospisilova et al., 2021). Liu et al. have utilized EESI to measure the particle-phase products formed from $^{\bullet}$OH heterogeneous oxidation of organophosphate flame retardants and liquid crystal monomers in real-time, to study their toxicological mechanism on photooxidation (Liu, Liggio, et al., 2019; Liu et al., 2020). Besides, EESI-MS was often combined with gas-phase analytical approaches to characterize the formation and evolution of SOA in laboratory research. Lamkaddam et al. demonstrated that over half of isoprene oxidation products partitioned into the cloud droplets and were further oxidized, leading to the formation of in-cloud aqueous SOA, by determining the particle bulk molecular composition using EESI-MS and the gaseous composition using PTR-TOF and NO_3^--CIMS (Lamkaddam et al., 2021). Because of the capability to detect aerosols with a large range of particle sizes, EESI-MS has also been used to study the molecular composition of ultrafine particles as small as 20 nm from naphthalene or β-caryophyllene oxidation (Surdu et al., 2021).

In contrast to that EESI-MS is used in both ambient aerosol composition studies and laboratory SOA composition, the other ambient ionization mass spectrometry such as DART-MS has been more often used to measure laboratory aerosol composition in multiphase chemistry, such as the heterogeneous oxidation of model OA systems, including multifunctional carboxylic acids (Chan et al., 2014; Cheng et al., 2015, 2016; Chim et al., 2017; Davies & Wilson, 2015; Lam, Shum, et al., 2019), alkenes (Lee & Wilson, 2016; Schwartz-Narbonne et al., 2019; Zhou et al., 2016), organosulfates (Kwong, Chim, Davies, et al., 2018; Kwong, Chim, Hoffmann, et al., 2018; Lam, Kwong, et al., 2019; Xu, Ge, et al., 2020). In most of these studies, the comprehensive molecular characterization of the oxidation products by DART-MS allowed for elucidation of the OA heterogeneous oxidation mechanisms. In addition, the quantitative nature of DART-MS measurements also make it possible to use the kinetic results to help understand the effects of aerosol phase state (Chan et al., 2014), aerosol viscosity (Davies & Wilson, 2015), and organic-inorganic mixing (Lam, Shum, et al., 2019).

In addition to the aerosol bulk composition, it is often important to also understand the surface composition of aerosol particles, especially when it is different than that of the aerosol bulk. The surface chemistry provides unique insights in aerosol formation and evolution, helping better understanding their impacts on air quality, human health, and atmospheric climate. In fact, the above-described DART-MS was first reported to be a surface-sensitive technique, when not assisted by sample vaporization (Davies & Wilson, 2015; Nah et al., 2013; Zhao, Fairhurst, et al., 2017). For example, Zhao et al. studied the multiphase reactions between submicron diacid particles and gas-phase amines, proposing that DART-MS probes ~30 nm the surface layer of the particles (Zhao, Chan, et al., 2017). Using this technique, the surface composition of SOA from α-cedrene oxidation were characterized (Figure 13) (Zhao, Chan, et al., 2017). Besides DART-MS, the ambient SSI mass spectrometry and the inlet ionization mass spectrometry are also powerful approaches to uniquely identify the surface molecular components of OA in the atmosphere. Wingen and Finlayson-Pitts and Qin et al. has utilized these techniques to study the surface compositions of organic particles using model OA and SOA systems, providing new insights into aerosol surface composition, chemistry, and gas-particle interactions (Qin et al., 2022; Wingen & Finlayson-Pitts, 2019).

3.4 | Isomer-level identification and quantification

Atmospheric organic constituents are largely comprised of structural isomers, from VOCs to low-volatility species in aerosols (Goldstein & Galbally, 2007). Thus, resolving the atmospheric organic mixtures on the isomeric level is crucial for understanding reaction kinetics, chemical mechanisms, and environmental impacts. The GC preseparation process before mass spectrometry analysis

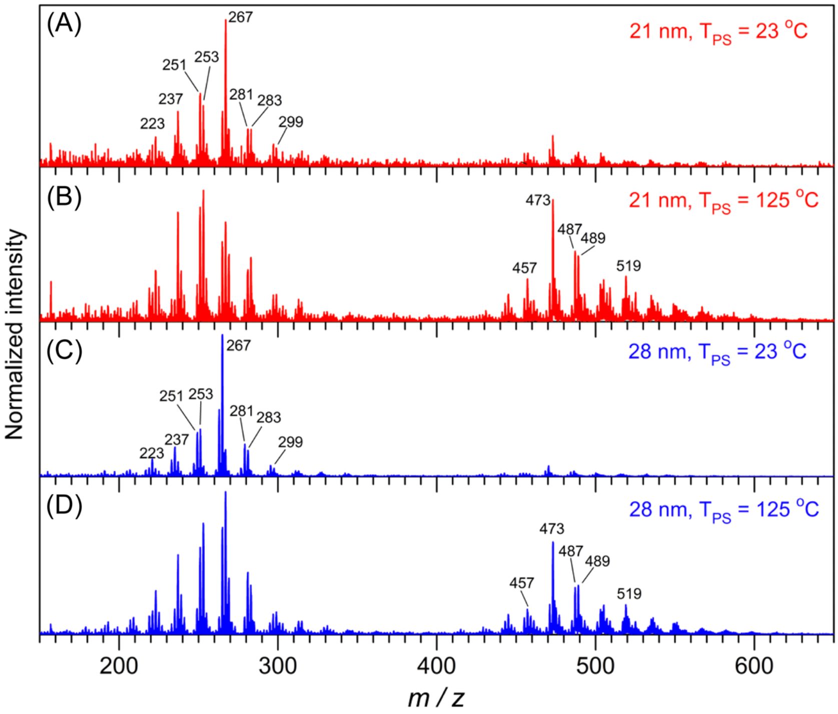

FIGURE 13 DART-MS mass spectra of polydisperse α-cedrene SOA particles with surface weighted geometric mean diameters of 21 nm (A, B) and 28 nm (C, D) at particle stream temperatures (T_{PS}) of 23°C and 125°C. Reproduced with permission Zhao et al. (2017). Copyright 2017 Zhao et al. DART-MS, direct analysis in real-time-mass spectrometry; SOA, secondary organic aerosol. [Color figure can be viewed at wileyonlinelibrary.com]

has the ability to offer unique retention time for isomers, leading to the potential of GC-CIMS in detecting isomeric distributions derived from the oxidation of diverse atmospheric species. GC-CIMS using CF_3O^- as the reagent ion has been largely used in these applications to unravel the reaction kinetics, oxidation products, and reaction mechanisms. For example, Teng et al. resolved the gas-phase isomeric hydroxy nitrates that are formed via reactions of $NO + RO_2^{\bullet}$ derived from OH-initiated oxidation of isoprene to quantify the $RO_2^{\bullet}$ isomerization rates and the reversible conversion between alkyl radical and $RO_2^{\bullet}$ (Figure 14) (Teng et al., 2017). Vasquez et al. used the same technique and showed that different isoprene-derived hydroxy nitrate isomers have distinct hydrolysis rates and hence different effects on NO_x recycling (Vasquez et al., 2020b). Kurtén et al. suggested that nitrate radical oxidation of α-pinene favors the formation of volatile pinonaldehyde via bond scissions of nitrooxy alkoxy radicals over low-volatility organonitrate by experimentally quantifying the isomeric hydroperoxyl nitrates using GC-CF_3O^--CIMS and computationally calculating the barriers and rate constants of the different bond scission pathways (Kurtén et al., 2017). In addition to biogenic VOC oxidation processes, the isomer-resolved identification and quantification of dominated phenol and hydroxy nitrates from the oxidation of bicyclic $RO_2^{\bullet}$ radicals in the presence of NO have implied the new benzene oxidation mechanism under atmospheric conditions (Xu, Møller, et al., 2020). Other regent ions such as NO^+ and its hydrated ion $NO{\cdot}H_2O^+$ were developed in the positive mode of GC-CIMS to characterize less oxygenated compounds, such as, non-methane organic gaseous isomers from biomass burning via GC-NO^+-CIMS (Koss et al., 2018), and benzene and its oxidation product glyoxal via GC-$NO{\cdot}H_2O^+$-CIMS (Xu, Møller, et al., 2020).

Iodometry-assisted LC-ESI-MS has been a helpful method to separate and distinguish organic peroxide isomers. As has been mentioned earlier, isomer-resolved characterization of peroxide monomers and dimers produced from α-pinene ozonolysis was achieved by this technique (Yao et al., 2022). In this work, a total of 75 organic peroxides were observed in α-pinene-derived SOA via iodometry-assisted LC-ESI-MS in both the positive and negative ion modes. Meanwhile, the varied abundance of most organic peroxides during the evaporation process suggested the significance to develop a comprehensive technique in aerosol chemistry to identify molecular structure of peroxide isomers and other atmospheric species. In the study by Zhao et al., α-acyloxyalkyl hydroperoxides as organic peroxides formed via stabilized Criegee intermediates from α-pinene ozonolysis reacting with carboxylic acids were identified using iodometry-assisted LC-ESI-MS (Zhao et al., 2018b). They determined the total organic peroxide content in α-pinene SOA and reported a lower total mass yield than previous work using the spectroscopic method, which could be explained by the rapid decomposition or inefficient ionization in LC-ESI-MS for certain peroxides (Badali et al., 2015; Docherty et al., 2005; Epstein et al., 2014; Li et al., 2016; Mertes et al., 2012; Wang et al., 2011). This group further utilized the technique to characterize isomer-resolved molecular composition of α-pinene and isoprene oxidation, including identifying isomer-resolved dimer esters derived from acyl $RO_2^{\bullet}$ during α-pinene ozonolysis (Zhao, Yao, et al., 2022),

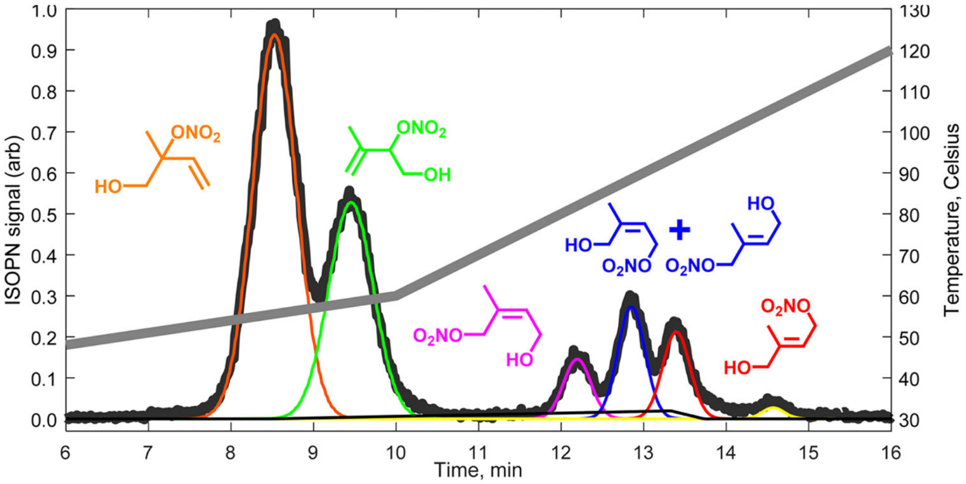

FIGURE 14 The distribution of isoprene hydroxynitrate isomers from isoprene photooxidation measured by the Caltech GC-CIMS. These isomers are separated using GC and detected as a cluster ion with CF_3O^- observed at m/z 232 Th. The grey line shows the GC oven temperature as a function of time. Reproduced with permission Teng et al. (2017). Copyright 2017 American Chemical Society. GC-CIMS, gas chromatography-chemical ionization mass spectrometer. [Color figure can be viewed at wileyonlinelibrary.com]

measuring C_5–C_{20} isomeric species during the oxidation of isoprene and monoterpene mixtures (Wang et al., 2021), and investigating the hydrolysis stability of individual peroxide compounds (Liu et al., 2022).

The IMS-MS could separate isomeric compounds based on ion mobilities by providing a unique drift time of each isomer at the same mass-to-charge ratio, indicating its ability to resolve structural isomers which are otherwise challenging to be distinguished in typical mass spectrometry measurements. In the study carried out by Krechmer et al., three isomers of hydroxy sulfate ester derived from the reactive uptake of IEPOX onto wet acidic sulfate aerosols were characterized over distinct drift times by IMS-MS (Krechmer et al., 2016). Further studies have used this capability to demonstrate OA compositional evolution during aging (Zhao, Le, et al., 2019) and heating (Zhao, Yang, et al., 2020) on the isomeric level. In addition, by comparing with the ion mobilities of authentic standards, oxidation products during heterogeneous $^{\bullet}OH$ oxidation of model OA compounds can be structurally verified, hence providing important insights into the multiphase oxidation mechanisms (Figure 15) (Zhao, Mayorga, et al., 2020). Lastly, the IMS-MS was used to distinguish actual dimers with covalent bonds from artifact clusters resulted from ESI by monitoring the dimer ion fragmentation with increased collision-induced dissociation voltage (Zhao, Tolentino, et al., 2019). This led to the first report of dimer formation during heterogeneous $^{\bullet}OH$ oxidation of OA. Most of these above-mentioned IMS-MS applications were possible owing to the additional mobility separation. Otherwise, the formula-level measurements and potential matrix effects in typical ESI-MS would make the findings challenging to explain.

4 | CURRENT ISSUES AND FUTURE DIRECTIONS

In this review, we summarized new developments of mass spectrometry techniques in the field of atmospheric chemistry and their applications to identify and quantify a broad range of atmospheric chemicals in both the gas and particle phases. Although these new developments have made unprecedented advancements in understanding atmospheric composition and processes, a few unsolved issues still remain. In this section, we discuss these issues and possible future developments to further advance the field of atmospheric chemistry.

4.1 | Instrument artifacts

Despite versatile CIMS development with new IMR designs and various reagent ions, a remaining issue is the measurement artifacts. The artifacts may arise from a number of physical and chemical processes. First, the interactions between relatively low-volatile analytes and instrument inner walls, such as absorption or desorption processes, have been suggested to contribute to negative or positive artifacts in measured chemical concentrations (Palm et al., 2019; Rivera-Rios et al., 2014). Second, chemical reactions may occur in the sample inlets. For example, artifacts were found by different air sampling

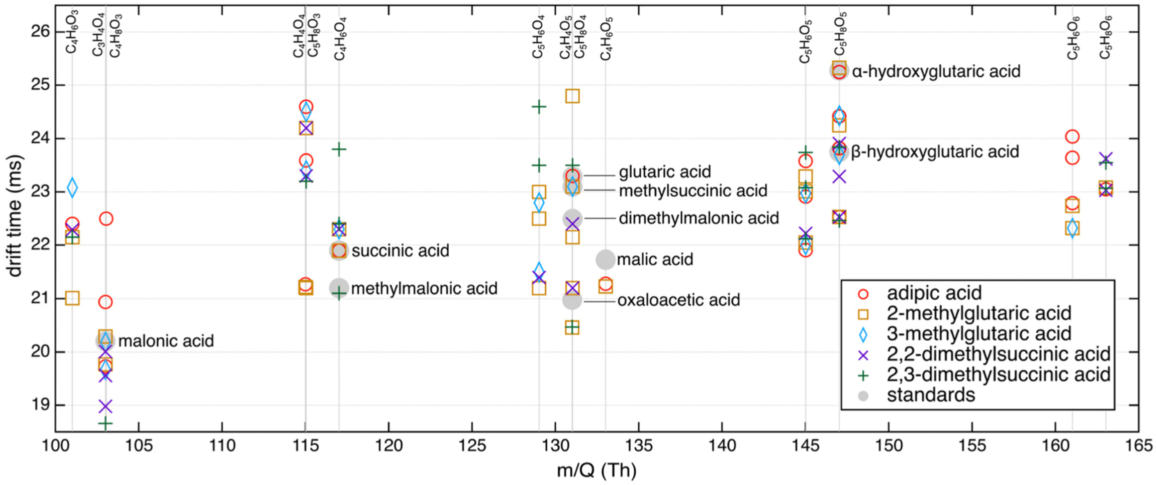

FIGURE 15 IMS-MS drift time—*m*/*z* diagram of major fragmentation products in the heterogeneous oxidation of five studied OA systems (see legend). The drift times of relevant available chemical standards are labeled, helping identifying oxidation products. Reproduced with permission Zhao et al. (2020). Copyright 2020 American Chemical Society. IMS-MS, ion mobility spectrometry–mass spectrometry; OA, organic aerosols. [Color figure can be viewed at wileyonlinelibrary.com]

configurations due to the reactions between air samples and overloading filters (Koss et al., 2018; Liu, Deming, et al., 2019). Third, secondary chemistry between components in the IMR during chemical ionization may cause interference to chemical composition analysis. Dörich et al. reported the biased detection of HNO_3 as NO_3^- in the presence of peroxyacetic nitric anhydride (PAN), peroxyacetic acid and O_3 using I^--CIMS (Dörich et al., 2021). Zhang et al. further proposed the interactions between a strong oxygen donor such as O_3 or peracids and acidic organics such as carboxylic acids or organic hydroperoxides in the IMR region of I^--CIMS, causing the formation of monomer and dimer iodide adducts to interfere the measurement of molecular compositions (Zhang & Zhang, 2021). In addition, Bernhammer et al. reported secondary reactions between organic precursors in the PTR3 reaction chamber that interference the measurements of isoprene-derived HOMs and might cause an overestimation of both the nucleation rate and the growth rate (Bernhammer et al., 2018). Last but not least, fragmentation of chemicals or ions may occur for certain ionization chemistries. For instance, Li et al. showed that the commonly observed peroxide dimers using many CIMS techniques were found to have small signals in Vocus PTR-TOF, because the protonation in PTR leads to fragmentation of such compounds (Li et al., 2022). However, as we described earlier, many of the same dimers were successfully measured by PTR3 (Figure 8), despite its similar ionization technique with Vocus PTR-TOF (Breitenlechner et al., 2017). The contrasting results may suggest that the dimer fragmentation in Vocus PTR-TOF could be caused by other reasons rather than protonation. Further investigation is warranted.

In addition to the artifacts for gas-phase CIMS measurements, a common problem in characterizing particle-phase compounds using vaporization-based methods is thermal decomposition (Lopez-Hilfiker et al., 2015; Stark et al., 2017; Thompson et al., 2017; Yang et al., 2021). More importantly, thermal decomposition was found to occur even at moderately heated temperatures for multifunctional compounds (Zhao, Yang, et al., 2020). For the ESI-based techniques that apply minimal heating, artifact may also exist. In particular, ESI has been known to generate microdroplets with charges at the surface, where chemistry could occur at much faster rates than in the bulk (Anglada et al., 2020; Banerjee & Zare, 2015; Jacobs et al., 2019; Ruiz-Lopez et al., 2020). It is thus unclear whether some of the products observed via ESI-MS could be formed during ESI, rather than in the intrinsic aerosol processing. Another uncertainty is whether the entire microdroplet or aerosol sample is probed by ESI and EESI. Some previous studies have reported that ESI-MS only sample the outermost surface layers of the microdroplet (Colussi & Enami, 2019). We suggest these questions to be carefully investigated in future research to better understand the measurements of atmospheric aerosol molecular composition.

4.2 | Quantification of complex organic mixtures

Accurate quantification using mass spectrometry remains a major challenge for atmospheric organic species, especially for the oxygenated molecules without authentic standards. The CIMS sensitivities depend on a number of factors, including the ion-molecule reaction rate, the yield of the product ion, the stability and transmission efficiency of the product ion, IMR temperature, relative humidity, electric fields, and so forth. As a result, it is challenging to constrain the sensitivities using physically based models (Iyer et al., 2016). Such complex dependence could be simplified to some extent by the selection of ion chemistry and the design of IMR, allowing the sensitivities to be controlled by fewer factors.

The sensitivities of some instruments have been shown to be proportional to the ion-molecule reaction rate constants. These instruments include CF_3O^--CIMS, PTR-MS, and NO_3^--CIMS (Garden et al., 2009; Paulot et al., 2009; Sekimoto et al., 2017). In CF_3O^--CIMS, the ion-molecule reaction is in the kinetic-limited regime, as the reaction time is on the order of 1 ms, enabled by the transverse IMR in the Caltech CIMS. The reaction time in PTR-MS is even shorter (i.e., ~0.1 ms) because of the drift voltage. In addition, the protonated ions produced from the proton transfer reactions are stable in the electric fields. In NO_3^--CIMS, even though the reaction time is relatively long (~200 ms), the analyte•NO_3^- cluster is extremely stable and does not break apart in the electric fields, so that it is often assumed that the analytes charges are at their collision frequency with NO_3^- (Ehn et al., 2014). The ion-molecule reaction rate constants, which are essential to constrain the sensitivities under this condition, can be calculated based on analyte dipole moment and polarizability (Garden et al., 2009), estimated based on the analyte molecular mass, elemental composition, and functional group (Sekimoto et al., 2017), assumed at collision limit (Hansel et al., 2018), or considered to be the same as another analyte which can be experimentally calibrated (Bernd, Richters, et al., 2016; Bianchi et al., 2019; Ehn et al., 2014; Guo, Yan, et al., 2022; Jokinen et al., 2015; Molteni et al., 2018; Rissanen et al., 2019).

Instead of ion-molecule reaction rate constants, the controlling factor of sensitivities in some CIMS is the stability of product ion. This applies to the IMR design in which the ion-molecule reactions are in thermodynamic equilibrium because of the long reaction time (~100 ms in I^--CIMS; Lee et al., 2014, $C_6H_6^+$-CIMS; Kim et al., 2016, and $(C_2H_5OH)H^+$-CIMS; Yu & Lee, 2012) or when a strong declustering electric field exists (e.g., NH_4^+-CIMS; Xu et al., 2022a; Zaytsev, Breitenlechner, et al., 2019). To constrain the sensitivity, the stability of product ion can be experimentally estimated using the voltage scanning tests, in which the change in the product ion signal is monitored in response of a systematic change in the voltage gradient between two ion optics (Lopez-Hilfiker et al., 2016; Xu et al., 2022a; Zaytsev, Breitenlechner, et al., 2019). However, the uncertainties of this approach could be substantial, as a recent study by Bi et al. showed that this method may carry uncertainties on the order of 0.5 to 1 magnitude for individual analytes in I^--CIMS (Bi et al., 2021b).

In addition to intrinsic properties of IMR, an environmental factor affecting CIMS sensitivity is the relative humidity. The sensitivities of a vast majority of analytes in most CIMS show dependence on relative humidity. The relative humidity can increase or decrease the sensitivity by affecting the distribution of reagent ion clusters and product ions, stabilizing the ion clusters with in-excess collision energy, affecting the transmission of water-soluble gases, and other mechanisms (Iyer et al., 2016; Lee et al., 2014). Such water dependence largely complicates the quantification. It is an active research area to minimize the relative humidity dependence. For example, Vocus deliberately adds a large amount of water vapor into the IMR, such that the variation in ambient relative humidity causes minimal disturbance in the IMR and the water dependence in both H_3O^+ and $NH_4{\bullet}H_2O^+$ chemistry is negligible (Krechmer et al., 2018; Xu et al., 2022b).

The quantification challenge is further compounded by the fact that atmospheric organic species are often very complex mixtures, enriched with isomers. Yet, many of the above-described mass spectrometry techniques cannot separate isomers. To explore the isomer-dependent sensitivities, Bi et al. coupled a TAG-CIMS using I^- to a quantitative flame ionization detector (FID) and reported that in I^--CIMS measurements an average number of three to five isomers were found per chemical formula (Bi et al., 2021a), but the isomers' sensitivities could vary by a maximum of 2 orders of magnitude (Bi et al., 2021b).

The quantification issues may be more challenging for particle-phase organics using ambient ionization mass spectrometry. For example, although the analyte response and sensitivity in EESI-MS is less affected by changing OA matrix compared to traditional infusion ESI systems, individual species have different sensitivities by a factor of 30 or more (Lopez-Hilfiker et al., 2019). In contrast, in the study by Brown et al., although the measured signals using EESI-MS are correlated and comparable with those measured by FIGAERO-CIMS, the relative sensitivities to various compounds change by a factor of 100 (Brown et al., 2021). During an aircraft measurement, Pagonis et al. showed that variability of EESI-MS calibration factor is 60% (1σ), implying further concerns of the quantitative capability of EESI-MS in field studies (Pagonis et al., 2021). Moreover, the characteristic of corona discharge in DART-MS prevents the potential of precise quantitative assays due to the lack of enough desorption and ionization information (Brüggemann et al., 2015; Feider et al., 2019). Very limited efforts have been made to quantify speciated OA compounds using other ambient ionization techniques (Kenseth et al., 2020).

4.3 | Bias caused by selectivity of ionization methods

Besides the challenges to quantify organic species in complex atmospheric mixtures, it is important to point out that selectivity of ionization methods can often cause bias for molecular analysis of these complex mixtures qualitatively and quantitatively. As described earlier, the HOM formation yield from α-pinene + OH may have very different results by using NO_3^--CIMS versus $CH_3C(O)O^-$-CIMS (Berndt, Richters, et al., 2016; Ehn et al., 2014). In another example, it was reported that very different light-absorbing chromophores in biomass burning OA were determined using ESI versus atmospheric pressure photoionization (Lin et al., 2018). These results suggest that multiple complementary ionization methods need to be applied to the same sample or same reaction system for more comprehensive characterization.

4.4 | Real-time characterization of structures or functional groups

In recent years, the focus of real-time mass spectrometry developments has been to improve mass resolution, sensitivity, and the range of detectable compounds. It remains challenging to inform chemical structures or functional groups during these measurements. Complementary analysis could fill the gap on this aspect, such as the iodometry-assisted LC-MS (Yao et al., 2022; Zhao, Kenseth, Huang, Dallaeska, Kuang, et al., 2018; Zhao, Kenseth, Huang, Dallaeska, & Seinfeld, 2018; Zhao, Yao, et al., 2022), IMS-MS (Krechmer et al., 2016; Zhang et al., 2019; Zhao, Tolentino, et al., 2019; Zhao, Yang, et al., 2020), and spectrophotometric methods (Aimanant & Ziemann, 2013; Ranney & Ziemann, 2016, 2017). However, most of these approaches are offline, particle-bound focused, and require sample collection, extraction, and so forth. It would be helpful to develop continuous sampling approaches and auxiliary platform methods to covert the "offline" mode to an "online" mode for the above techniques. The information regarding chemical structures and functional groups in real-time would greatly benefit mechanistic understanding of processes in both the gas and particle phases. Recently, online derivatization methods have been designed to couple with AMS for determining particle-phase peroxides based on redox reactions (Weloe & Hoffmann, 2020): supersaturated gaseous triphenylphosphine is continuously added to mix with SOA samples in the front of AMS inlet, and the formed triphenylphosphine oxide is then monitored and quantified by AMS with a time resolution of 2 min. By combining with such online derivatization method, the real-time peroxide quantification in the SOA could be achieved. It is anticipated that other derivatization techniques could be developed for soft ionization mass spectrometry to provide functional group information.

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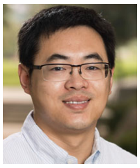

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