



Revisiting benzene cluster cations for the chemical ionization

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Revisiting benzene cluster cations for the chemical ionization of dimethyl sulfide and select volatile organic compounds

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Abstract

Benzene cluster cations were revisited as a sensitive and selective reagent ion for the chemical ionization of dimethyl sulfide (DMS) and a select group of volatile organic compounds (VOCs). Laboratory characterization was performed using both a new set of compounds (i.e. DMS, β -caryophyllene) as well as previously studied VOCs (i.e., isoprene, α -pinene). Using a field deployable chemical ionization time-of-flight mass spectrometer (CI-ToFMS), benzene cluster cations demonstrated high sensitivity ($> 1 \text{ ncps ppt}^{-1}$) to DMS, isoprene, and α -pinene standards. Parallel measurements conducted using a chemical-ionization quadrupole mass spectrometer, with a weaker electric field, demonstrated that ion-molecule reactions likely proceed through a combination of ligand-switching and direct charge transfer mechanisms. Laboratory tests suggest that benzene cluster cations may be suitable for the selective ionization of sesquiterpenes, where minimal fragmentation ($< 25\%$) was observed for the detection of β -caryophyllene, a bicyclic sesquiterpene. The field stability of benzene cluster cations using CI-ToFMS was examined in the marine boundary layer during the High Wind Gas Exchange Study (HiWinGS). The use of benzene cluster cation chemistry for the selective detection of DMS was validated against an atmospheric pressure ionization mass spectrometer. Measurements from the two instruments were highly correlated ($R^2 = 0.80$) over a wide range of sampling conditions.

1 Introduction

Volatile organic compounds (VOCs) play a central role in atmospheric chemistry by regulating tropospheric ozone and secondary organic aerosol (SOA) production rates (Goldstein and Galbally, 2007). Global emissions of non-methane VOCs are dominated by biogenic VOCs (BVOCs) such as terpenes, where isoprene (C_5H_8) and monoterpenes (MT; $\text{C}_{10}\text{H}_{16}$) emissions have been shown to be most significant (Arnold et al., 2009). Recent studies have shown that sesquiterpenes (SQT; $\text{C}_{15}\text{H}_{24}$) may also play

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a significant role in SOA production (Jaoui et al., 2013 and others), but far less is known about their global emission rates (Guenther et al., 2012; Kanakidou et al., 2005). In one of the few studies with simultaneous measurements of isoprene, MT, and SQT (Kim et al., 2009) inferred ecosystem scale fluxes that suggest that SQT fluxes could be as much as 50 % that of MT in deciduous forests (Kim et al., 2009). In terrestrial regions, the condensable oxidation products of terpenes have been shown to drive SOA production, particularly in boreal and sub-tropical forests (Guenther et al., 2012). In comparison, SOA precursors in the marine boundary layer have historically been thought to be dominated by dimethyl sulfide (DMS) emissions, with isoprene and monoterpenes contributing less than 1 % to SOA mass (Myriokefalitakis et al., 2010).

Chemical ionization mass spectrometry (CIMS) is increasingly utilized as a fast, sensitive and selective measurement technique for in situ detection of reactive trace gas species (Huey, 2007). The benefits of CIMS are most pronounced when sampling from moving platforms or during instrumentally-tasking sampling methods such as eddy covariance, where high time resolution is required. Proton transfer mass spectrometry (PTR-MS) has been used extensively for the sensitive, selective determination of VOCs providing direct measurements of concentrations and turbulent fluxes from a variety of mobile platforms (e.g., Lindinger et al., 1998). PTR-MS is well suited for the measurement of small molecules such as DMS and isoprene, but fragmentation of larger volatile organic compounds, such as monoterpenes and sesquiterpenes, can limit accuracy (Kim et al., 2009). In parallel, separation techniques (e.g., gas chromatography) have been utilized to detect BVOCs with good sensitivity and the added benefit of resolving isobaric interferences at both nominal and fragment masses (Helmig et al., 2004). However, low temporal resolution limits their utility for higher time resolution analyses. In what follows, we extend the early work of Leibrock and Huey (2000) to explore the utility of benzene cluster cations, $(C_6H_6)_n^+$, for the selective, sensitive and rapid detection of various SOA precursors via chemical ionization mass spectrometry (CIMS) in the marine boundary layer.

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The use of benzene cations as selective reagent ions dates back to at least the work of Horning et al. (1973), where trace benzene vapor was introduced into an atmospheric pressure ionization mass spectrometer. As discussed by Horning, benzene ion chemistry was thought to proceed through either a charge transfer Reaction (R1) if the ionization energy (IE) for the analyte (A) was less than that of benzene (9.24 eV) or through a proton transfer Reaction (R2) if the gas phase basicity of the analyte (B) is greater than that of the phenyl radical:



Horning et al. demonstrated that large, complex organics (e.g., testosterone) could be detected with minimal fragmentation as the molecular ion (M^+), while 2,6-dimethyl- γ -pyrone was detected as MH^+ following Reaction (R2). It is thus expected that an array of gas-phase bases (e.g., amines) could be detected using this ion chemistry. With specific application to atmospheric chemistry, Ketkar et al. (1991) revisited benzene ion chemistry for the selective detection of 2-chloroethyl ethyl sulfide.

The most complete and recent work on benzene ion chemistry with application to atmospheric measurements is from work by Leibrock and Huey, where the potential for benzene cations in the detection of isoprene and monoterpenes, among a suite of other conjugated dienes and aromatics. Leibrock and Huey (2000) demonstrated that select VOCs with ionization energies lower than that for benzene (9.24 eV) react at or near the collision limit either via direct charge transfer Reaction (R1) forming the molecular cation X^+ or through a ligand switching reaction involving the benzene dimer cation Reaction (R3) forming the ion-neutral cluster $\text{X}^+(\text{C}_6\text{H}_6)$. It is likely that if ionization proceeds through Reaction (R3), the number of molecules that can be detected will be reduced as the ionization energy for the benzene dimer cation has been measured to be significantly less (ca. 8.6 eV) than the monomer (Grover et al., 1987).



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It follows that benzene ion chemistry should be a sensitive measurement for a host of molecules of interest to the study of marine air, including dimethyl sulfide (DMS) (IE = 8.6 eV), monoterpenes (IE = 8.07 eV, α -pinene), sesquiterpenes (IE = 8.3 eV, β -caryophyllene) and their first generation oxidation products, as well as a host of atmospheric amines through Reaction (R2) (Al-Joboury and Turner, 1964; Hunter and Lias, 1998; McDiarmid, 1974). Further, due to the high density of states of C_6H_6 and $(C_6H_6)_2$, collisional energy from the ion-molecule reaction can be readily absorbed, permitting the efficient formation of weakly bound ion-neutral clusters and the potential for very soft ionization of large BVOCs such as bicyclic sesquiterpenes.

These advantages are not without potential challenges: (1) like many positive ion CIMS techniques, extensive dehydration of alcohols can complicate the interpretation of mass spectra. Specifically, Leibrock and Huey showed that the dehydration of 2-methyl-3-buten-2-ol (MBO), could lead to a positive artifact in the detection of isoprene, despite the fact that the IE for MBO exceeds 9.24 eV, (2) benzene ion chemistry is not exceedingly selective as compared with other ion-molecule chemistries, as such the potential for interferences in low mass resolution instruments is high, particularly in polluted air-masses, and (3) while it is not expected that benzene cations will directly ionize water, it has been shown that under high specific humidity, benzene cations may have a series of attached water molecules (Ibrahim et al., 2005; Miyazaki et al., 2004) that may introduce a water dependence in the ion chemistry.

In what follows, we describe laboratory characterization experiments and field observations in the remote marine boundary layer to assess the utility of benzene cations for the detection of DMS and select BVOCs. Laboratory experiments were conducted using both a chemical-ionization time-of-flight mass spectrometer (CI-ToFMS) (Bertram et al., 2011) and a chemical ionization quadrupole mass spectrometer (CI-QMS) to probe ion-molecule reaction mechanisms and adduct stability under different electric field strengths. Field measurements from the remote North Atlantic boundary layer were validated against simultaneous measurements of DMS made by an atmospheric

pressure ionization mass spectrometer with an isotopically labeled standard (APIMS-ILS) (Blomquist et al., 2010).

2 Experimental

2.1 Instrument descriptions

The utility of benzene reagent ion chemistry for the sensitive, selective detection of DMS, isoprene, and monoterpenes was characterized on two CIMS instruments: (1) a field deployable chemical ionization time-of-flight mass spectrometer (CI-ToFMS; Tofwerk AG and Aerodyne Research Inc.) (Bertram et al., 2011) optimized for the sensitive detection of trace gases from mobile platforms and (2) a laboratory based chemical ionization quadrupole mass spectrometer (CI-QMS) operated without declustering optics or ion guides, achieving low electric field strengths at the cost of sensitivity. Despite different ion transmission optics and mass analyzers, the two instruments utilize identical ion-molecule reaction chambers.

2.1.1 Chemical ionization time of flight mass spectrometer (CI-ToFMS)

A complete description of the CI-ToFMS hardware can be found in Bertram et al. (2011). Briefly, reagent ions are generated by passing benzene gas diluted in ultra-high purity (UHP) N_2 through an α -emitting polonium source (Sect. 2.1.3), then mixed with ambient air in an ion-molecule reaction (IMR) chamber ($P_{IMR} = 70$ mbar). Reaction times are estimated to be on the order of 100 ms, significantly longer than the time scale for ion-molecule reactions to reach equilibrium. Product ions pass through four additional differentially pumped stages, beginning with the collisional dissociation chamber ($P_{CDC} = 2$ mbar) housing an RF-only quadrupole ion guide. In the CDC, ion-molecule adducts can be dissociated by adjusting the electric field strength or pressure of the chamber. Ions are then passed through the second RF-only quadrupole ion guide housed at 1.4×10^{-2} mbar, and then a chamber containing final focusing optics

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that condition the ion beam for entry into the extraction region of the ToF mass analyzer, where ions are orthogonally extracted into a compact time-of-flight mass spectrometer (Tofwerk AG and Aerodyne Research Inc.). Typical extraction frequencies range between 30–85 kHz resulting in mass spectra spanning between 11–319 m/Q . Individual mass spectra are averaged and saved at 10 Hz following the procedures outlined in Bertram et al. (2011).

2.1.2 Chemical ionization quadrupole mass spectrometer (CI-QMS)

The CI-QMS used in these studies employs the same ion molecule reaction chamber described in Bertram et al. (2011), but operated at a different pressure ($P_{\text{IMR}} = 100$ mbar). In contrast to the CI-ToFMS, the CI-QMS was operated to minimize the declustering of weakly bound ion-neutral clusters prior to detection. The CI-QMS was operated with only three stages of differential pumping and with a series of lenses in place of the RF ion guide devices. The resulting instrument achieves minimal collisional declustering at the expense of sensitivity. Ions were mass selected using a quadrupole mass analyzer (Extrel Inc.). Transmitted ions were detected using a continuous dynode and electron multiplier, where single ion events were converted to TTL pulses for measurement and analysis via custom LabView software. The CI-QMS was operated in parallel with the CI-ToFMS to provide insight into the ion cluster distributions at the point of reaction as the stronger electric fields, and subsequent dissociation of ion-neutral clusters in the CI-ToFMS limit the ability to monitor ion chemistry occurring in the IMR.

2.1.3 Reagent ion generation and chemistry

On both platforms, the reagent ion precursor (benzene gas) was generated by diluting a certified compressed gas standard (150 ppm \pm 0.1 ppm in N_2 , Praxair) with UHP N_2 generated from LN_2 boil off. The total reagent flow rate is limited by an inline critical orifice (1.8 slpm) which also serves the additional purpose of keeping permeable

Teflon tubing at positive pressure relative to the atmosphere to prevent diffusion of contaminants into the ion generation lines. Downstream of the orifice, gas flow is passed through a α -emitting polonium-210 source (NRD 2021–1000 at 10 mCi initial activity). N_2^+ ions are formed via electron transfer reactions with α -particles (Reaction R4) and go on to ionize neutral benzene (Grover et al., 1987) to form a distribution of benzene cations $(C_6H_6)_n^+$ ($n = 1, 2, \dots$) (Reactions R5 and R6).



3 Laboratory characterization

3.1 Factors controlling primary ion distributions

During laboratory experiments, the CI-QMS and CI-ToFMS ion generation systems were identical with the exception of the IMR pressure. As shown in Fig. 1, the benzene ion distribution as measured by CI-QMS was detected predominantly in the form of $(C_6H_6)_2^+$ at 156 m/Q (Fig. 1a). The same gas mixture was detected by CI-ToFMS in the form of $C_6H_6^+$ at 78 m/Q (Fig. 1b). This suggests that the reagent ion distribution primarily exists as $n \geq 2$ in the CI-ToFMS IMR as well, but the field strength of the RF-only quadrupole ion guide in the CDC of the CI-ToFMS exceeds the benzene dimer binding energy of 15.3 kcal mol⁻¹ (Grover et al., 1987) despite operating at a relatively weak field strength. Unfortunately, even in the CI-QMS, significant declustering occurs between the IMR and the mass analyzer. As a result, it is not possible to comment directly on the distribution of benzene cluster cations in the IMR and the possibility that the clusters may have attached water molecules. However, based on the CI-QMS spectra, the clusters are at least dimers ($n \geq 2$) in both instruments.

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3.1.1 Dependence on benzene reagent gas concentration

Background mass spectra were examined by overflowing the sample inlet with UHP zero air while varying the concentration of benzene delivered through the ionizers of both the CI-ToFMS and the CI-QMS instruments. The relative humidity at the sample inlet was less than 5% during these experiments. On the CI-ToFMS, the benzene monomer accounted for 68–91% of the total ion current (Fig. 2) for benzene precursor ion concentrations ranging between 1–45 ppm. Peak benzene ion signal intensities were found at benzene reagent gas concentrations of approximately 10 ppm. At lower benzene concentration (< 10 ppm), a wide array of background ions are prevalent in the mass spectra. Although the zero air cylinders were assumed to be nominally dry, trace amounts of water (detected as protonated water clusters) were evident in the sample stream at low benzene concentrations. At higher benzene concentrations (> 10 ppm) background peaks at 92, 106 and 120 m/Q become an increasing fraction of the total ion current. At 10 ppm benzene, these ions collectively account for 1–3% of total ion current. During HiWinGS underway measurements, the sum of these three peaks comprised an average of 2.6% ($1\sigma = 0.8\%$) of the total ion current. These background peaks were observed across all CIMS instruments, and their strength increased with benzene concentration (Fig. 2) suggesting they are trace contaminants in the benzene cylinders. We provisionally attribute these peaks to toluene, ethylbenzene, xylene, and trimethylbenzene.

As shown in Fig. 3, the ratio of benzene cation dimer-to-monomer was approximately $1 : 10^4$ on the CI-ToFMS and $3 \times 10^3 : 1$ for the CI-QMS. The presence of the dimer in the CI-ToFMS mass spectrum provides additional evidence that the reagent ion distribution primarily exists as $n \geq 2$ in both of the IMRs, but the field strength of the RF-only quadrupole ion guide in the CDC of the CI-ToFMS exceeds the benzene dimer binding energy of 15 kcal mol^{-1} (Grover et al., 1987).

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3.1.2 Dependence on ambient humidity

Ambient humidity was varied to probe its impact on ion chemistry and product ion distributions. In this experiment, benzene reagent gas concentrations were held at 10 ppm while sampling humid UHP zero air (0–100 % relative humidity, room temperature). On the CI-ToFMS, benzene monomers remained > 86 % of the total ion current (Fig. 4a) at 100 % relative humidity (RH), compared with 91 % at < 1 % RH. Absolute benzene monomer count rates showed minimal sensitivity to ambient water vapor (Fig. 4b). Protonated water clusters ($\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$) were observed upon the addition of water vapor to sample air. The sum of the ion current for $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ($n = 0-3$) ranged from 0.7–8.5 % of the total ion current, increasing with relative humidity. Again, trace amounts of water vapor were detected while sampling nominally dry UHP zero air (Praxair) due to a small amount of condensation in zero air cylinders.

Given that the ionization energy of benzene (9.2 eV monomer, 8.69 eV dimer) (Nemeth et al., 1993) is less than water (12.6 eV) (Page et al., 1988), it is unlikely that a benzene mediated pathway for the formation of protonated water clusters is active. Additionally, since benzene-water clusters are not observed, it is possible that protonated water clusters may be formed by direct ionization (Good et al., 1970) due to back diffusion of ambient water into the Po-210 source, or persistent N_2^+ from the ionizer may contribute to direct ionization of water downstream in the IMR. Similarly, molecular oxygen ions (O_2^+ , 12.0 eV) (Tonkyn et al., 1991) from ambient air are observed in trace amounts (< 1.3 % of the total ion current). Despite the fact that benzene-water clusters were not observed in the mass spectra, we have no direct evidence that they are not present in the IMR and they may impact instrument sensitivity, as described in Sect. 3.4.

3.2 Instrument calibration

Calibration curves were generated using three parallel CIMS systems (CI-ToFMS, CI-QMS, and CIMS that employs a residual gas analyzer for ion selection and quantifi-

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cation, CI-RGA) to determine the sensitivity of benzene cations to dimethyl sulfide, isoprene, and α -pinene. Results from the first two instruments are included here. Results from the CI-RGA will be discussed in a forthcoming manuscript. Calibration factors were determined using atmospherically relevant mixing ratios (0–3.2 ppb) of dimethyl-^{1,1,1-d₃} sulfide (Praxair certified standard, 0.184 ppm \pm 10 %), isoprene (Praxair certified standard, 0.500 ppm \pm 10 %) and α -pinene (Praxair certified standard, 0.497 ppm \pm 10 %) at specific humidities (q) from 0 to 16.6 g kg⁻¹. The primary VOC calibration standards were diluted with ultra-high purity (UHP) zero air (Praxair). Humidified buffer gas was generated by flowing UHP zero air through three sequential frit bubblers (Ace Glass) containing deionized water. Flow rates for all VOC standards and both the dry and saturated dilution flows were measured using mass flow meters or mass flow controllers (\pm 10 %). A mass closure calculation was performed during portions of the experiments using measured flow rates and saturation vapor pressures to ensure the humidified air stream was fully saturated. Bubbler temperatures were recorded for specific humidity calculations accounting for cooling at very high flow rates due to gas expansion. All CIMS instruments were positioned around a central manifold (0.635 cm OD PFA tube and 0.635 cm PFA Swagelok fittings) and sampled from its own radial branch. Humidified air was added furthest downstream to minimize the surface area exposed to condensation. Each inlet branch was the same length to within 5 cm. Excess flow was directed from the central manifold line to an exhaust at atmospheric pressure.

Benzene cations were demonstrated to be sensitive to isoprene and α -pinene (Fig. 5) in agreement with previous work by Leibrock and Huey (2000), as well as DMS. Normalized sensitivities (normalized counts per second per ppt or ncps ppt⁻¹) were calculated by adjusting product ion count rates to a reference reagent ion signal of 10⁶ cps (Warneke et al., 2001). Thus, absolute sensitivity increases with benzene ion current. Calibration factors are reported as the slope of the linear fit of each calibration curve (1σ = slope standard deviation). Maximum normalized sensitivities were as follows: DMS (23.5 ncps ppt⁻¹), α -pinene (41 ncps ppt⁻¹), and isoprene (8.3 ncps ppt⁻¹).

All three VOCs calibration factors exhibited unique humidity dependences described in more detail in Sect. 3.3.

3.3 Adduct declustering

VOC product ions were detected at nominal mass (M^+) or as a benzene adduct ($(C_6H_6)^+$). On both the CI-QMS (Fig. 1a) and CI-ToFMS (Fig. 1b) isoprene was detected as an adduct (146 m/Q), while α -pinene appeared at nominal mass (136 m/Q). The former indicates that isoprene ionization proceeds through a ligand switching reaction. For the latter, this result suggests that α -pinene may also undergo a ligand switching mechanism with subsequent disassociation during transmission or alternatively may be ionized via direct charge transfer.

In contrast, dimethyl-1,1,1- d_3 sulfide was detected predominately as M^+ (65 m/Q) on the CI-ToFMS and as a benzene-DMS adduct (143 m/Q) on the CI-QMS. This indicates that DMS ionization proceeds through a ligand-switching reaction in both instruments, but the adduct dissociates in the stronger declustering fields of the CI-ToFMS. Despite attempts to minimize the field strength of the CI-ToFMS, we were not able to observe the DMS-benzene cluster.

Instrument response to pure, yet unquantified mixing ratios of a host of other VOCs, including a sesquiterpene and a monoterpene, were assessed with the CI-ToFMS. In these experiments a small volume (1 mL) of pure β -caryophyllene and eucalyptol standards were deposited into clean flasks and their vapors were delivered to the CI-ToFMS inlet. Product ions were identified and normalized (%) to the sum of all feasible products. As described previously, DMS and α -pinene product ions appear at M^+ (99 and 83% respectively), while isoprene is detected primarily as a benzene adduct (88%) (Fig. 6). β -caryophyllene was detected as M^+ (204 m/Q) with very limited fragmentation (< 25%). Since β -caryophyllene has been demonstrated to fragment more readily than other sesquiterpenes (Kim et al., 2009), these tests suggest that benzene dimer cations show excellent promise as an accurate chemical ionization method to target easily fragmented terpene species. Eucalyptol (1,3,3-Trimethyl-2-

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oxabicyclo[2,2,2]octane), an oxygenated monoterpene (C₁₀H₁₈O) was also detected as M⁺ (154 *m/Q*) with limited fragmentation (Fig. 6). However, due to the proton affinity of eucalyptol (Maleknia et al., 2007), a secondary ionization reaction was evident at the M-H⁺ channel (see Sect. 1.2). After accounting for isotopic contributions, we estimate the ratio of charge transfer to proton transfer product ions are about 2 : 1 at ambient RH for eucalyptol.

3.4 Impact of ambient humidity on sensitivity

The sensitivity of benzene cluster cations to DMS, α -pinene, and isoprene standards was shown to be a strong function of specific humidity (q) (Fig. 5), with peak sensitivity occurring at specific humidities of 6.7 g kg⁻¹ (DMS, 23 ncps ppt⁻¹), 11.7 g kg⁻¹ (α -pinene, 41 ncps ppt⁻¹), and 11.7 g kg⁻¹ (isoprene, 8.3 ncps ppt⁻¹). Sensitivity varied with ambient specific humidity on all CIMS platforms. On the CI-ToFMS, DMS was observed to be least sensitive to changes in ambient water vapor, while α -pinene sensitivity increased almost linearly for q values between 0–11.7 g kg⁻¹.

At present, we do not have a definitive interpretation of the water dependence. While we do not observe a benzene-water cluster in any of our instruments, it is likely that the cluster exists in the IMR and is broken apart in the ion optics between the IMR and the mass analyzer. Results from Ibrahim et al., show that the stepwise binding energies for attaching a water molecule to C₆H₆⁺ are on the order of 8.5 kcal mol⁻¹, suggesting that the water molecules are removed via collisions in the transfer optics. Laboratory studies have shown previously that benzene-water clusters [C₆H₆-(H₂O)_{*n*}]⁺ can be made efficiently ($n = 1–23$) (Miyazaki et al., 2004). For large clusters ($n \geq 4$) IR spectra of the clusters suggest features that are nearly identical to protonated water clusters, suggesting exclusion of benzene and the formation of an attached water cluster. For smaller clusters ($n \leq 3$), IR spectra were shown to be consistent with a hydrated benzene cation, where benzene retains over 90 % of the charge (Ibrahim et al., 2005). It is likely that the sensitivity dependence we observe in these experiments depends on the location of the charge (benzene vs. water) and the size of the benzene-water clus-

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orifice (low pressure side), sample flow is split into a bypass (ca. 2.5 slpm) and sample (ca. 10 slpm) stream. The bypass branch is in-line with the manifold intake. The sample flow follows a series of 90° and 180° turns, which serve to eliminate super-micrometer sea spray particles from the sample inlet stream. The manifold was housed in an insulated, weather-proofed housing and mounted off the foremast. The sample intake was ca. 20 m above mean sea level (a.m.s.l.) and ca. 17 m aft of the bow (Yang et al., 2014). The sample line and manifold was heated by a PID heating circuit (Omega) set to 40 °C.

The inlet assembly comprised of a sample (0.95 cm OD FEP), bypass 0.635 cm OD PFA), baseline (0.95 cm OD FEP) and calibration (0.318 cm OD FEP) line running between the manifold and a temperature controlled instrument van housing the CI-ToFMS on the 02 deck. Baseline and calibration gas flows were controlled by mass flow controllers operated by an automated LabView program. Ambient sample air was pulled through the sample line to the front block, an additional differentially pumped chamber upstream of the CI-ToFMS IMR and held at the inlet assembly pressure (200 mbar). The CI-ToFMS subsampled from the front block, while the rest of the flow rejoined the bypass flow downstream of the instrument. Choked flow conditions in the entire manifold-inlet-front block volume were maintained by a 500 L min⁻¹ scroll pump (Varian TriScroll 600). Inlet assembly pressures were recorded by a Pirani pressure gauge on the front block. UHP zero air and VOC standards were added to the inlet manifold via separate ports located upstream of the critical orifice (i.e. high pressure side) to account fully for all surface losses to the manifold and inlet surfaces. Instrument baselines were determined by overflowing the manifold critical orifice with 20 slpm of UHP zero air from a gas tank (Praxair). VOC sensitivity was assessed with several daily standard additions and calibrations. The first three weeks of the research cruise utilized isoprene standards before switching to α -pinene during the last two weeks. For both calibrations, a 0.500 ppm primary standard in N₂ (Praxair) was used to achieve a constant 638 ppt mixing ratio in the inlet.

4.2 Inlet time response

Ambient VOC signal decays resulting from zero air additions were examined to characterize the inlet's time response (Fig. 7). Fitting a double exponential curve to signal decays yields two characteristic time constants for the inlet (Ellis et al., 2010). The first exponential decay time, τ_1 , is attributed the gas evacuation time and related to the physical operation and characteristics of the inlet itself. The second exponential decay time, τ_2 , is attributed to the equilibration constant of the gas itself and related to its polarity and solubility. For the $n = 1$ protonated water cluster ($\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$), τ_1 of 3.2 s agreed well with the volumetric evacuation time of 3.6 s at 12.56 slpm. The second characteristic time, τ_2 , was long for the protonated water cluster at 22 s, as expected based on the polarity and high surface affinity of water vapor. DMS and α -pinene also exhibited fast τ_1 time constants, but in contrast to H_2O , τ_2 time constants were also fast (1.2 and 2.5 s, respectively) indicating turbulent flow and minimal interaction of the analyte with the inlet walls.

4.3 Factors impacting reagent ion stability

Benzene reagent ion signal varied between 58–89% of the total ion current (8.02×10^5 to 6.4×10^6 cps benzene) during HiWinGS. Probability density functions of benzene counts during ambient and baseline periods each showed a bimodal distribution, but no difference from each other (Fig. 8). A similar trend in benzene ion current was observed during standard addition and calibration periods. Benzene ion signal shifted between the two modes several times over the course of the research cruise. Step-changes in benzene ion signal corresponded to days when reagent ion gas tanks were switched. Loss in benzene signal corresponded to nearly equal increases in protonated water cluster peaks (0.7–39% total ion current) and vice versa. These abrupt shifts occur independently of ambient specific humidity or other environmental variables. We suspect these shifts are driven by trace levels of condensation in the benzene standard cylinders or water vapor introduced into the gas delivery lines during cylinder exchange.

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During the previously described laboratory tests (Sect. 3.1.2), benzene remains $> 86\%$ and protonated water clusters peaked at 8.5% of total ion current at 100% relative humidity (Fig. 4a). At typical room temperatures ($20\text{--}24^\circ\text{C}$), 100% relative humidity is equivalent to specific humidities between $14.6\text{--}18.8\text{ g kg}^{-1}$. Minute average specific humidity during HiWinGS peaked at 13.2 g kg^{-1} , which suggests the large and abrupt increases in protonated water cluster signal (and corresponding decreases in benzene) are driven by water vapor in the reagent ion generation source, rather than ambient humidity. A less probable explanation for the increase in protonated water cluster signals may be attributed to diffusion of water into the permeable gas delivery lines that spanned over 30 m from the gas cylinder rack on the main deck to the instrument van on the 02 deck. Despite being sheathed, the lines were undoubtedly exposed to sea spray and condensation during large wave breaking. However, this would not explain the step-function changes in benzene and water signal over time. Future work will focus on the use of a liquid benzene reservoir that would not need to be exchanged during the course of the cruise.

4.4 In-field calibration and sensitivity

As expected, absolute sensitivity to VOC standard additions varied as a function of benzene reagent ion current and ambient water vapor. Calibration factors were calculated from raw count rates during each VOC addition after subtracting ambient contributions calculated from interpolating values from bracketed sampling periods. DMS calibration factors were derived from concurrent APIMS-ILS determined mixing ratios (cps ppt^{-1}) as discussed in detail below in Sect. 4.5. Mean absolute sensitivities were 19.4 , 2.8 and 6.1 cps ppt^{-1} for DMS, isoprene and α -pinene, respectively.

Instrument baselines are computed from the mean of raw count rates (1 Hz) measured during valid instrument zero periods throughout the entire campaign as in Kercher et al. (2009). Variability in baseline counts are largely driven by fluctuations in the benzene reagent ion current. Detection limits are calculated as in Bertram et al. (2011) as 3σ of a Gaussian fit for all baseline count rates over the entire cam-

paign. A conservative estimate of the CI-ToFMS detection limits, for 1 Hz sample averages were calculated to be 152, 13 and 42 ncps for DMS, isoprene and α -pinene, respectively (Table 1). Using sensitivities reported for $q = 6 \text{ g kg}^{-1}$, this corresponds to 1 Hz detection limits of 25, 15, and 14 ppt respectively.

After normalizing to the benzene ion count rate, the humidity dependence of in-field VOC normalized calibration factors (Fig. 9) is consistent with laboratory tests (Fig. 4), their values of normalized calibration factors were lower by a factor of 4–7 among individual VOCs, as highlighted for α -pinene in Fig. 10. Possible explanations include VOC standard degradation, inlet performance (less probable for nonpolar terpenes) or most likely due to shifts in sensitivity from tuning instrument voltages between the two experiments.

In deployments subsequent to the HiWINGS campaign, in-field calibrations have been performed utilizing continuous standard additions of isotopically labeled standards (when commercially available) as developed and used on several previous APIMS-ILS air–sea exchange campaigns (Bandy, 2002; Blomquist et al., 2010; Thornton, 2002).

4.5 Underway dimethyl sulfide comparison

Baseline adjusted, reagent-ion normalized count rates at $62 m/Q$ were compared to DMS mixing ratio measurements provided by the University of Hawaii's atmospheric pressure ionization mass spectrometer with isotopically labelled standard (APIMS-ILS). The instruments were housed in separate instrument vans on the 02 deck of the R/V *Knorr*. The CI-ToFMS sample manifold was mounted to the foremast as described in Sect. 4.1. The APIMS-ILS inlet was mounted to the meteorological mast located at the bow of the ship and ca. 16.3 m a.m.s.l. This is about 17 m fore and 4 m below the CI-ToFMS intake position.

Dimethyl sulfide baseline adjusted, normalized count rates were calculated by subtracting interpolated baseline values from ambient $62 m/Q$ counts and scaling to a benzene ion current of 10^6 cps (Warneke et al., 2001) (Fig. 11). No adjustments based on

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ambient humidity were made due to the lack of an active standard gas calibration. A regression analysis between the adjusted, normalized CI-ToFMS signal and APIMS-ILS DMS mixing ratio measurements showed excellent agreement ($R^2 = 0.80$) over extreme wind speeds, low ambient loadings, and temperatures below freezing (Figs. 11 and 12). This agreement between two independent DMS measurements lends confidence to the selectivity of both ionization methods and their robustness in the field. It also indicates both sampling locations were functionally equivalent and sampled air masses did not suffer from flow distortion around the superstructure of the ship. As suggested by laboratory tests, a slight water vapor dependence is evident at specific humidity higher than 10 g kg^{-1} but the calibration factor is largely constant over the humidity range ($1.6\text{--}12.8 \text{ g kg}^{-1}$) experienced during the cruise (Fig. 11).

5 Summary and future directions

Benzene cluster cations have been revisited as a chemical ionization method for the detection of DMS and select volatile organic compounds. DMS and β -caryophyllene were identified as novel VOC targets and product ions exhibited limited fragmentation. Sensitivity to DMS, isoprene, and α -pinene were determined using CI-ToFMS in laboratory experiments and in-field standard additions with a focus on humidity dependencies for performance in the remote marine boundary layer. Laboratory-based calibration factors ranged between 2 and 41 ncps ppt^{-1} with varying water vapor dependencies. These trends were well conserved between laboratory and field measurements, but normalized sensitivity values were lower in the field by a factor of 4–7. Minor background peaks attributed to alkyl-substituted benzene were traced to contamination in the benzene source. Water vapor in the benzene cylinder standards were also found to degrade benzene reagent ion signal during field operations. Future directions will explore the use of a liquid benzene reservoir that would not need to be exchanged during the course of the cruise and the potential extension of this ion chemistry beyond the select VOCs studied here.

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References

- Al-Joboury, M. I. and Turner, D. W.: Molecular photoelectron spectroscopy. Part II. A summary of ionization potentials, *J. Chem. Soc.*, 851, 4434–4441, 1964.
- Arnold, S. R., Spracklen, D. V., Williams, J., Yassaa, N., Sciare, J., Bonsang, B., Gros, V., Peeken, I., Lewis, A. C., Alvaïn, S., and Moulin, C.: Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol, *Atmos. Chem. Phys.*, 9, 1253–1262, doi:10.5194/acp-9-1253-2009, 2009.
- Bandy, A. R.: Determination of the vertical flux of dimethyl sulfide by eddy correlation and atmospheric pressure ionization mass spectrometry (APIMS), *J. Geophys. Res.*, 107, 4743, doi:10.1029/2002JD002472, 2002.
- Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M., and Worsnop, D. R.: A field-deployable, chemical ionization time-of-flight mass spectrometer, *Atmos. Meas. Tech.*, 4, 1471–1479, doi:10.5194/amt-4-1471-2011, 2011.
- Blomquist, B. W., Huebert, B. J., Fairall, C. W., and Faloona, I. C.: Determining the sea-air flux of dimethylsulfide by eddy correlation using mass spectrometry, *Atmos. Meas. Tech.*, 3, 1–20, doi:10.5194/amt-3-1-2010, 2010.
- Ellis, R. A., Murphy, J. G., Patey, E., van Haarlem, R., O'Brien, J. M., and Herndon, S. C.: Characterizing a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) for measurements of atmospheric ammonia, *Atmos. Meas. Tech.*, 3, 397–406, doi:10.5194/amt-3-397-2010, 2010.
- Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the earth's atmosphere, *Environ. Sci. Technol.*, 41, 1514–1521, 2007.

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- Grover, J., Walters, E., and Hui, E.: Dissociation energies of the benzene dimer and dimer cation, *J. Phys. Chem.*, 91, 3233–3237, 1987.
- Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5, 1471–1492, doi:10.5194/gmd-5-1471-2012, 2012.
- Helmig, D., Bocquet, F., Pollmann, J., and Revermann, T.: Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments, *Atmos. Environ.*, 38, 557–572, 2004.
- Horning, E. C., Horning, M. G., Carroll, D. I., Dzidic, I., and Stillwell, R. N.: New picogram detection system based on a mass spectrometer with an external ionization source at atmospheric pressure, *Anal. Chem.*, 45, 936–943, 1973.
- Huey, L. G.: Measurement of trace atmospheric species by chemical ionization mass spectrometry: speciation of reactive nitrogen and future directions, *Mass Spectrom. Rev.*, 26, 166–184, 2007.
- Hunter, E. P. L. and Lias, S. G.: Evaluated gas phase basicities and proton affinities of molecules: An update, *J. Phys. Chem. Ref. Data*, 27, 413, doi:10.1063/1.556018, 1998.
- Ibrahim, Y. M., Meot-Ner, M., Alshraeh, E. H., El-Shall, M. S., and Scheiner, S.: Stepwise hydration of ionized aromatics. Energies, structures of the hydrated benzene cation, and the mechanism of deprotonation reactions, *J. Am. Chem. Soc.*, 127, 7053–7064, 2005.
- Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg, J. H.: Secondary organic aerosol formation from the oxidation of a series of sesquiterpenes: α -cedrene, β -caryophyllene, α -humulene and α -farnesene with O_3 , OH and NO_3 radicals, *Environ. Chem.*, 10, 178–193, 2013.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.
- Kercher, J. P., Riedel, T. P., and Thornton, J. A.: Chlorine activation by N_2O_5 : simultaneous, in situ detection of $ClNO_2$ and N_2O_5 by chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 2, 193–204, doi:10.5194/amt-2-193-2009, 2009.

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Ketkar, S. N., Dulak, J. G., Dheandhanoo, S., and Fite, W. L.: Benzene charge exchange at atmospheric pressure for low-level detection of pollutants in ambient air, *Anal. Chim. Acta*, 245, 267–270, 1991.

Kim, S., Karl, T., Helmig, D., Daly, R., Rasmussen, R., and Guenther, A.: Measurement of atmospheric sesquiterpenes by proton transfer reaction-mass spectrometry (PTR-MS), *Atmos. Meas. Tech.*, 2, 99–112, doi:10.5194/amt-2-99-2009, 2009.

Leibrock, E. and Huey, L. G.: Ion chemistry for the detection of isoprene and other volatile organic compounds in ambient air, *Geophys. Res. Lett.*, 27, 1719–1722, 2000.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, *Int. J. Mass Spectrom.*, 173, 191–241, 1998.

Maleknia, S. D., Bell, T. L., and Adams, M. A.: PTR-MS analysis of reference and plant-emitted volatile organic compounds, *Int. J. Mass Spectrom.*, 262, 203–210, 2007.

McDiarmid, R.: Assignments of Rydberg and valence transitions in the electronic absorption spectrum of dimethyl sulfide, *J. Chem. Phys.*, 61, 274, doi:10.1063/1.1681633, 1974.

Miyazaki, M., Fujii, A., Ebata, T., and Mikami, N.: Infrared spectroscopy of size-selected benzene-water cluster cations $[C_6H_6 - (H_2O)_n]^+$ ($n = 1-23$): Hydrogen bond network evolution and microscopic hydrophobicity, *J. Phys. Chem. A*, 108, 10656–10660, 2004.

Myriokefalitakis, S., Vignati, E., Tsigaridis, K., Papadimas, C., Sciare, J., Mihalopoulos, N., Facchini, M. C., Rinaldi, M., Dentener, F. J., Ceburnis, D., Hatzianastasiou, N., O'Dowd, C. D., van Weele, M., and Kanakidou, M.: Global modeling of the oceanic source of organic aerosols, *Adv. Meteorol.*, 1–16, 2010.

Nemeth, G. I., Selzle, H. L., and Schlag, E. W.: Magnetic ZEKE experiments with mass analysis, *Chem. Phys. Lett.*, 215, 151–155, 1993.

Page, R. H., Larkin, R. J., Shen, Y. R., and Lee, Y. T.: High-resolution photoionization spectrum of water molecules in a supersonic beam, *J. Chem. Phys.*, 88, 2249–2263, 1988.

Thornton, D. C.: Fast airborne sulfur dioxide measurements by Atmospheric Pressure Ionization Mass Spectrometry (APIMS), *J. Geophys. Res.*, 107, 4632, doi:10.1029/2002JD002289, 2002.

Tonkyn, R. G., Wiedmann, R., Grant, E. R., and White, M. G.: Rotationally resolved photoionization of H_2O , *J. Chem. Phys.*, 95, 7033, doi:10.1063/1.461431, 1991.

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- 5 Yang, M., Blomquist, B. W., and Nightingale, P. D.: Air–sea exchange of methanol and acetone during HiWinGS: Estimation of air phase, water phase gas transfer velocities, *J. Geophys. Res.-Oceans*, 119, 7308–7323, 2014.

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Table 1. Summary of in-field CI-ToFMS performance on the HiWinGS research cruise for select volatile organic compounds. Isoprene and α -pinene were calibrated against in-field standards. DMS figures of merit utilized simultaneous, independent DMS mixing ratios from the University of Hawaii's APIMS-ILS. Limit of Detection (LOD) was calculated for 1 s averaging times using normalized sensitivities corresponding to $Q = 6 \text{ g kg}^{-1}$.

VOC Species	Sensitivity (1σ)	Background (1σ)	LOD (1 Hz, 3σ)
Dimethyl sulfide	$18.2 \pm 9.6 \text{ ncps ppt}^{-1}$	$636 \pm 389 \text{ cps}$	25 ppt
Isoprene	$0.7\text{--}1.1 \text{ ncps ppt}^{-1}$	$19.5 \pm 66 \text{ cps}$	15 ppt
α -Pinene	$0.8\text{--}6.3 \text{ ncps ppt}^{-1}$	$192 \pm 191 \text{ cps}$	14 ppt

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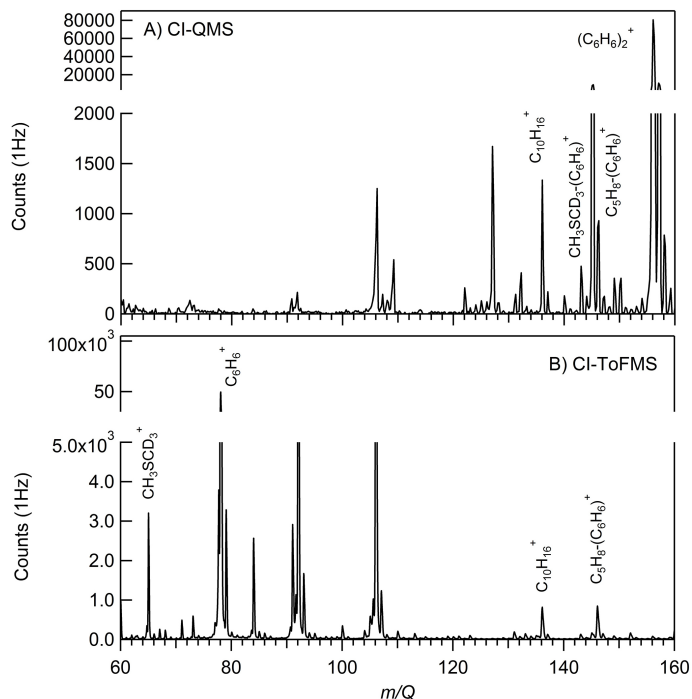


Figure 1. CI-QMS (a) and CI-ToFMS (b) mass spectra utilizing benzene reagent ion chemistry while sampling a mixture of dimethyl-1,1,1- d_3 sulfide, isoprene and α -pinene standards at 40 % relative humidity and room temperature. The weaker field strength of the CI-QMS transmits clustered forms of benzene ($(C_6H_6)_2^+$) and dimethyl-1,1,1- d_3 sulfide ($CH_3SCD_3-C_6H_6^+$). Both are detected at nominal mass by the CI-ToFMS. Isoprene is detected as a benzene cluster ($C_5H_8-C_6H_6^+$) and α -pinene ($C_{10}H_{16}^+$) appears at nominal mass on both instruments.

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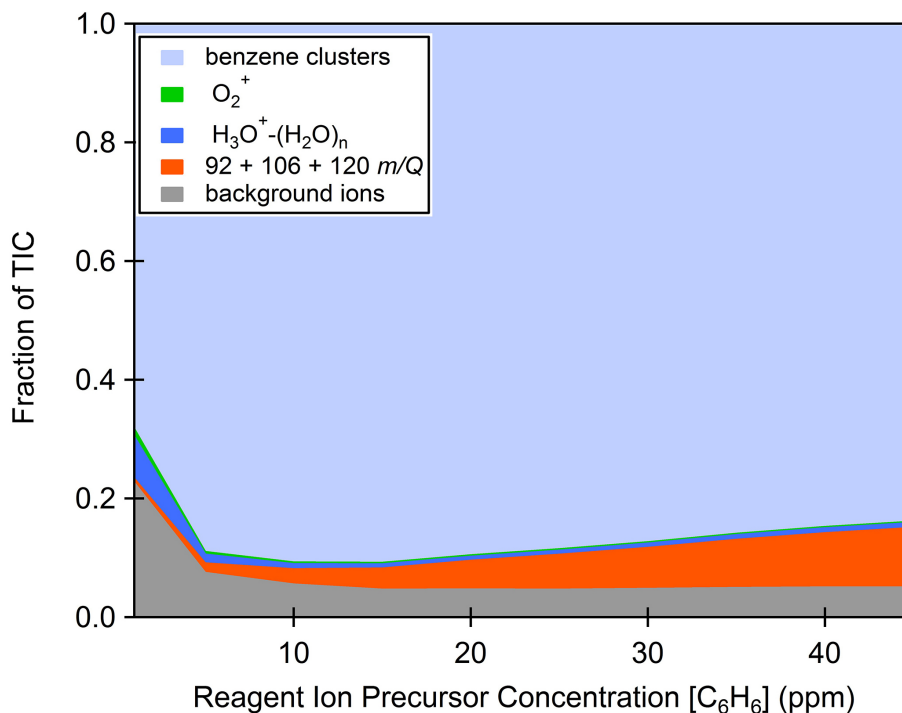


Figure 2. Partitioning of total ion current (TIC) on the CI-ToFMS between benzene clusters (light blue), O₂⁺ (green), water clusters (dark blue, $n = 0$ to 3), and background peaks (orange and grey) as a function of benzene reagent ion concentration at < 1% relative humidity. Molecules corresponding to 92, 106 and 120 m/Q are attributed to alkyl-substituted benzene molecules: C₆H₅-CH₃⁺, C₆H₄-(CH₃)₂⁺, and C₆H₄-(CH₃)₃⁺, respectively.

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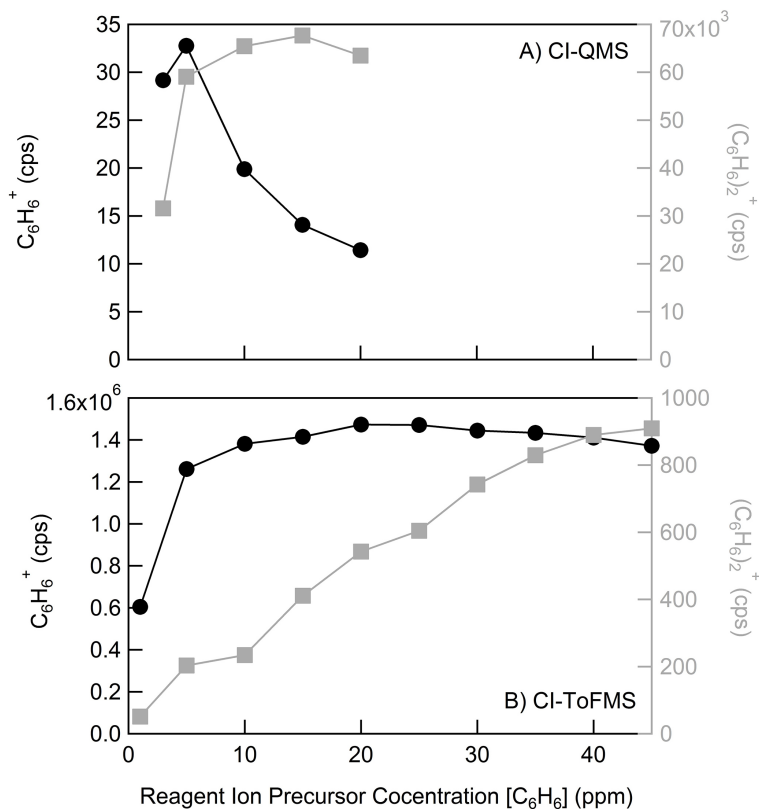


Figure 3. Dependence of benzene ion signal intensity on the benzene reagent gas concentration for both the CI-QMS (a) and CI-ToFMS (b). Nearly all CI-QMS benzene signal intensity is found at the dimer (156 m/Q) while the CI-ToFMS was nearly exclusively in the form of the monomer (78 m/Q). On both platforms, the dominant benzene peak plateau after 10 ppm neutral benzene concentration.

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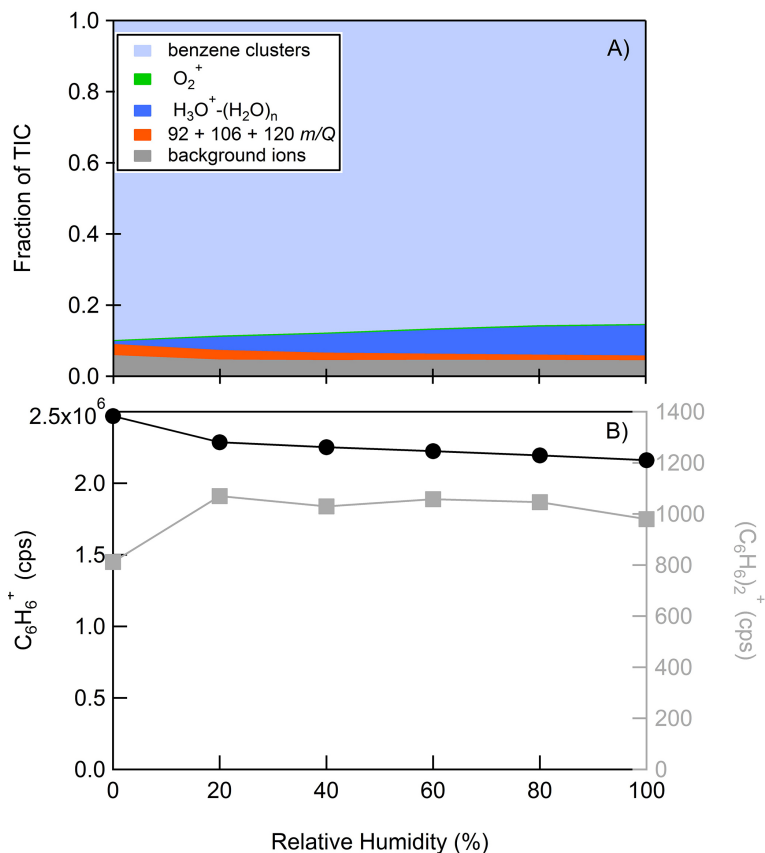


Figure 4. (top) Dependence of primary ion signal intensities and partitioning between the monomer and dimer on ambient relative humidity ($[C_6H_6] = 10\text{ ppm}$) on the CI-ToFMS. (bottom) Absolute benzene ion signal intensities are shown to be nearly independent of ambient relative humidity.

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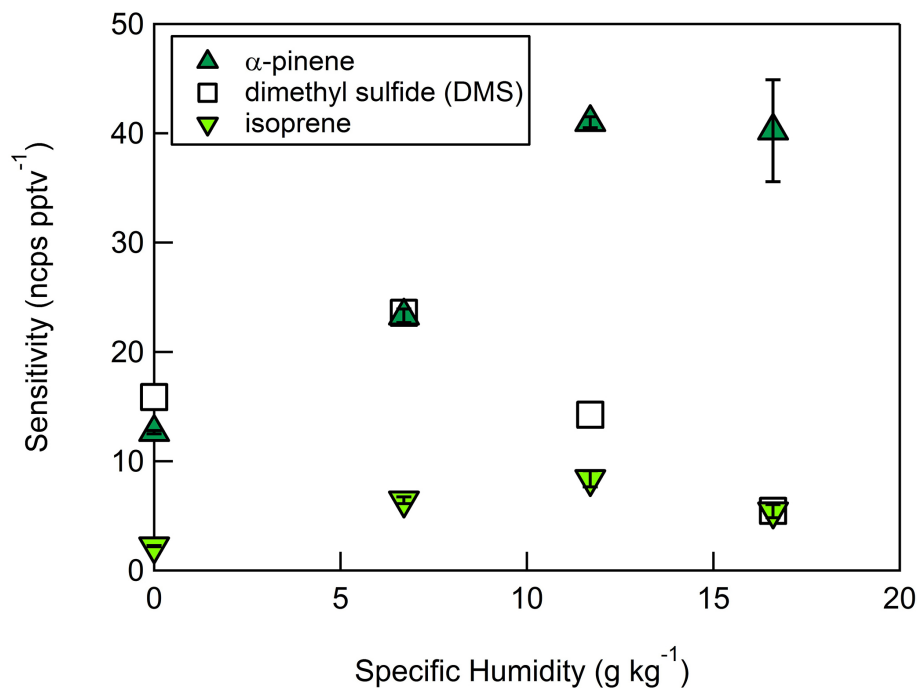


Figure 5. Humidity dependence of the laboratory derived CI-ToFMS sensitivities to dimethyl-1,1,1- d_3 sulfide, α -pinene, and isoprene. Error bars indicate 1σ as determined from the slope of the calibration curve.

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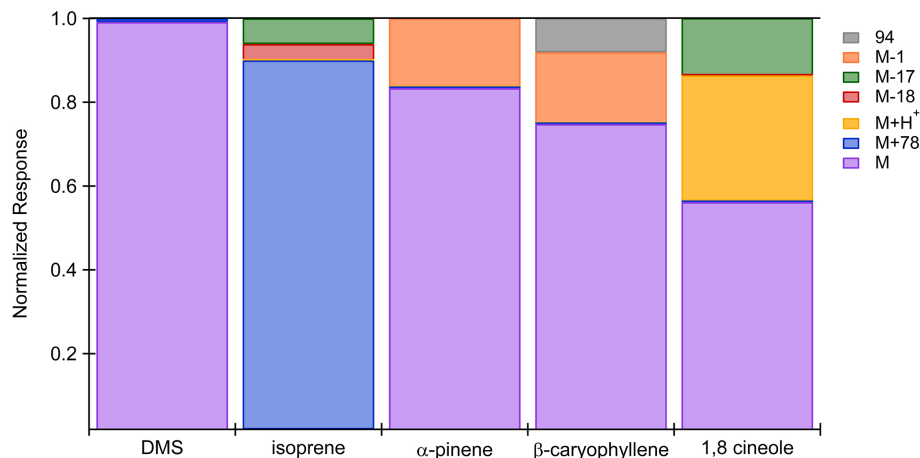


Figure 6. Normalized response of the CI-ToFMS to a series of VOC standards. Significant products (> 5% of instrument response) are shown for DMS, isoprene, α -pinene, β -caryophyllene, and eucalyptol (1,8-cineole). For eucalyptol, the ratio of charge transfer to proton transfer products were roughly 2 : 1. Expected isotopic contributions were accounted for in the calculated proton transfer products.

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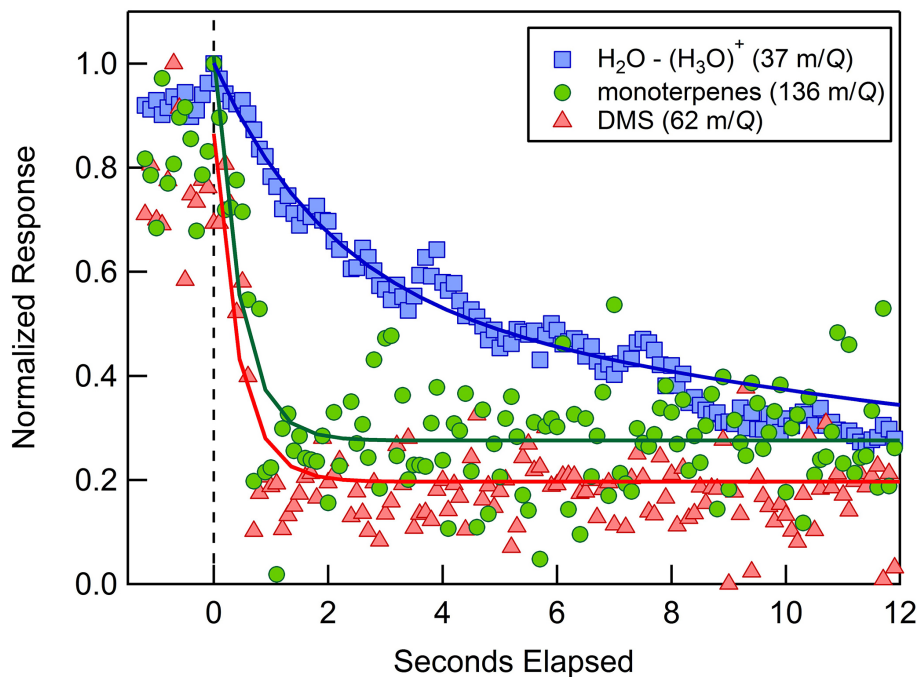


Figure 7. Inlet and instrument response to a prompt switch from ambient sampling to a zero air addition. The first rapid decay is attributed to the gas evacuation time (τ_1) and the second decay is attributed to the inlet wall-equilibration time (τ_2). Best fit estimates of τ_1 for H_3O^+ (H_2O), DMS, and monoterpenes ranged between 2 and 3 s, in agreement with the volumetric evacuation time of the sample inlet (3.6 s). τ_2 was determined to be 22, 1.2, and 2.5 s, respectively.

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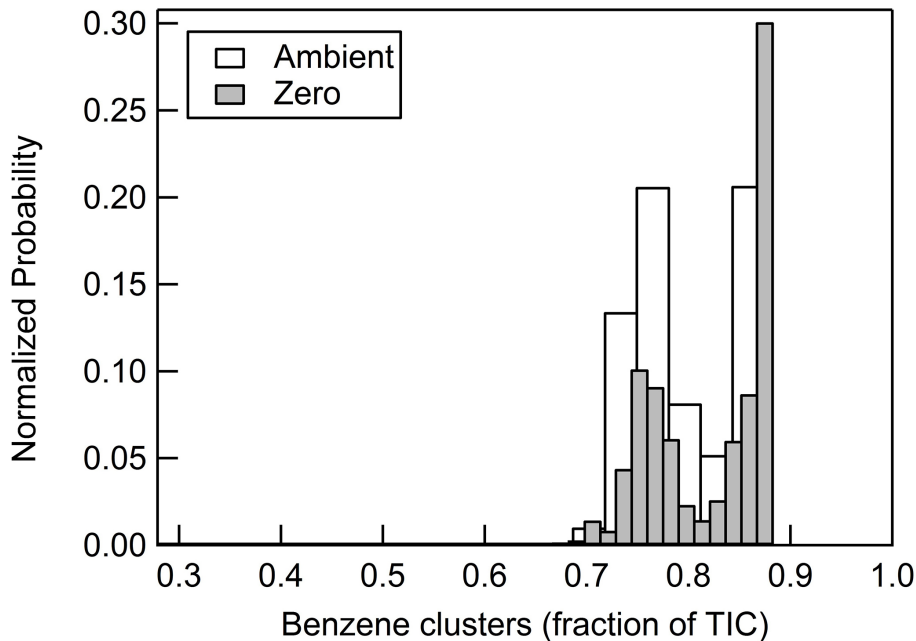


Figure 8. Probability density functions of benzene signals (% total ion current, 1 Hz) for ambient and baseline sampling periods. The bimodal distribution corresponds to abrupt temporal shifts in ion current from benzene monomers to protonated water clusters. These shifts correspond to switches in benzene gas cylinders rather than changes in ambient specific humidity, indicating the bimodal distribution is driven by trace water vapor contaminants in the benzene gas cylinders.

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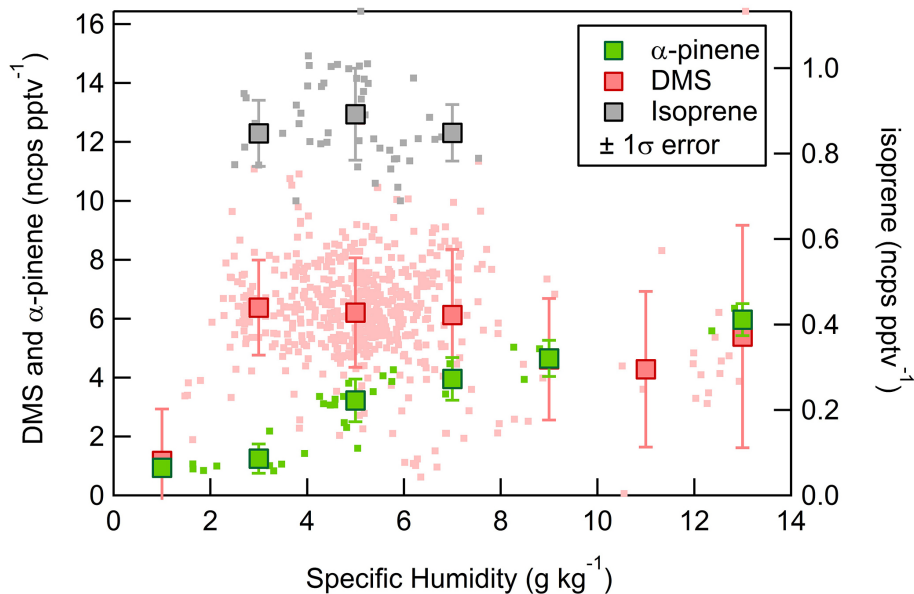


Figure 9. In-field sensitivities during standard additions as a function of ambient specific humidity. Dots represent hourly values while squares represent mean values for a 2 g kg^{-1} specific humidity bin.

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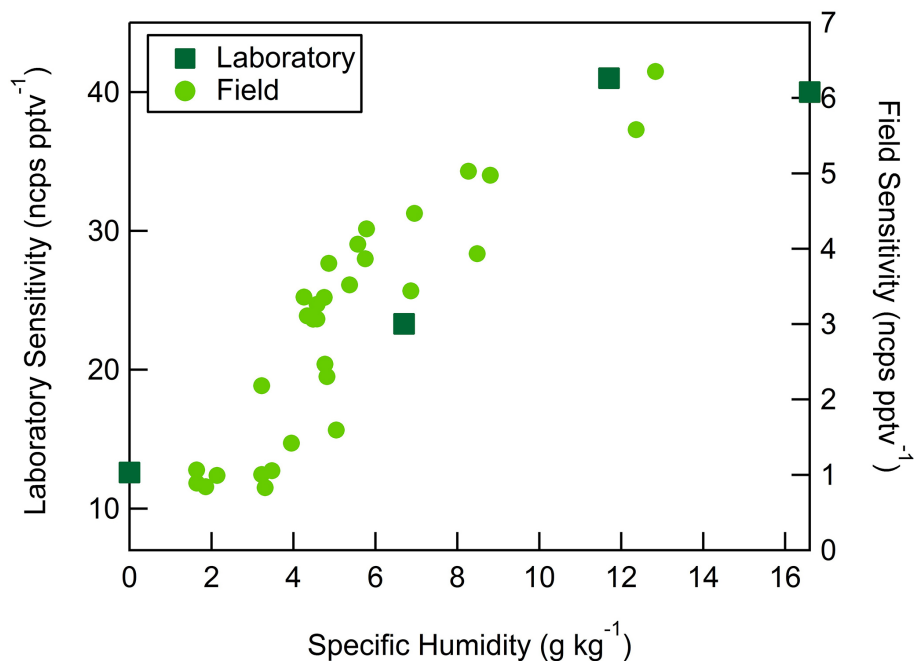


Figure 10. Comparison of α -pinene calibration factors observed during laboratory experiments (left axis) and during in-field standard additions (right axis). Similar dependence on specific humidity was observed.



Revisiting benzene cluster cations for the chemical ionization

M. J. Kim et al.

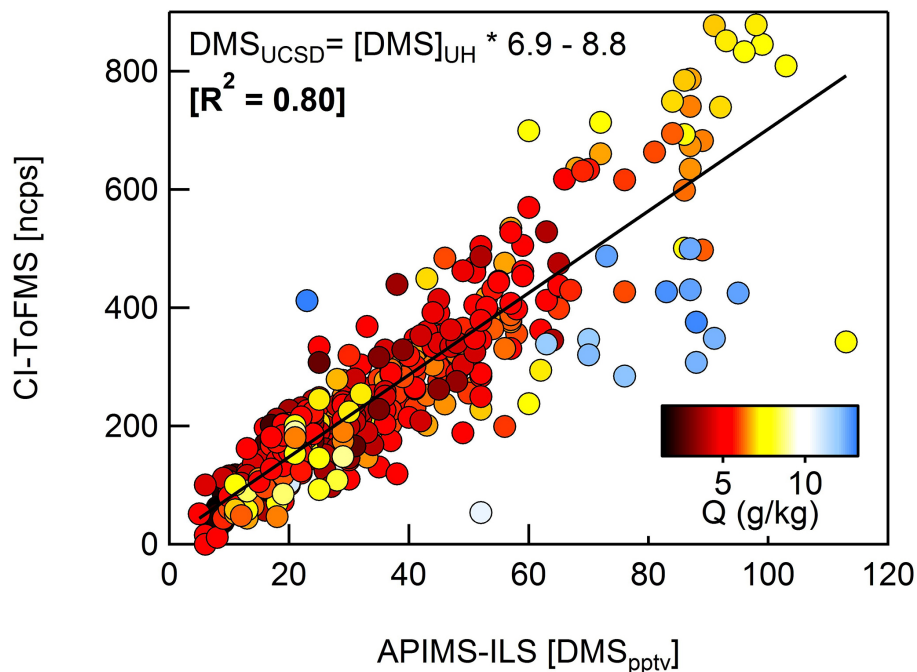


Figure 11. Regression of background corrected, benzene normalized DMS counts against DMS concentrations measured by APIMS-ILS. The regression indicates a campaign average CI-ToFMS sensitivity of $6.9 \text{ ncps ppt}^{-1}$. A slight humidity dependence is apparent for $q > 10 \text{ g kg}^{-1}$, which is supported by laboratory tests.

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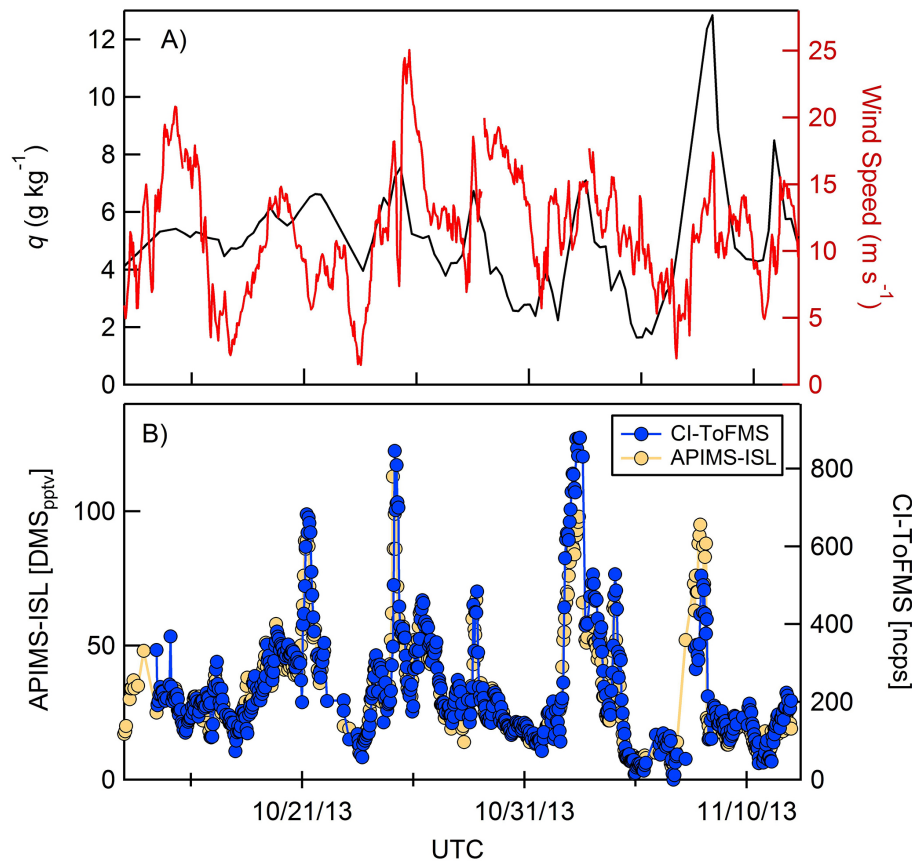


Figure 12. Hourly measurements from the High Wind Gas Exchange Study (HiWinGS) research cruise. Normalized CI-ToFMS count rates compared well ($R^2 = 0.80$) with dimethyl sulfide mixing ratios measured by the University of Hawaii APIMS-ILS. No corrections were made for ambient humidity.