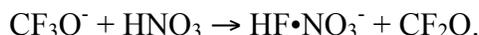
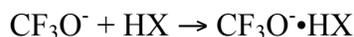


The Caltech CIMS instrument

The single mass analyzer CIMS (S-CIMS) was developed for use on NASA's ER-2 aircraft. Its first measurements were made in 2000 (SOLVE). Subsequently, it has flown on the NASA DC-8 aircraft for INTEX-NA, DICE, TC4, and ARCTAS, as well as on the NCAR C-130 during MILAGRO/INTEX-B. HNO_3 is measured by selective ion chemical ionization via the fluoride transfer reaction:



In addition to its fast reaction rate with HNO_3 , CF_3O^- can be used to measure additional acids and nitrates as well as SO_2 [Amelynck *et al.*, 2000; Crounse *et al.*, 2006; Huey *et al.*, 1996]. We have further identified CF_3O^- chemistry as useful for the measurement of less acidic species via clustering reactions [Crounse *et al.*, 2006; Paulot *et al.*, 2009a; Paulot *et al.*, 2009b; St. Clair *et al.*, 2010]:



where, e.g., $\text{HX} = \text{HCN}, \text{H}_2\text{O}_2, \text{CH}_3\text{OOH}, \text{CH}_3\text{C}(\text{O})\text{OOH}$ (PAA).

The mass analyzer of the S-CIMS instrument has recently been upgraded from a quadrupole to a time-of-flight (ToF) analyzer. The new configuration is shown in Figure 1, with the new mass analyzer shown in red. The ToF admits the sample ion beam to the ion extractor, where a pulse of high voltage orthogonally deflects and accelerates the ions into the reflectron, which in turn redirects the ions toward the multichannel plate detector. Ions in the ToF follow a V-shaped, 43 cm path from extractor to detector, separating by mass as the smaller ions are accelerated to greater velocities by the high voltage pulse. The detector collects the ions as a function of time following each extractor pulse. The rapid-scan collection of the ToF guarantees a high temporal resolution (1 Hz or faster)

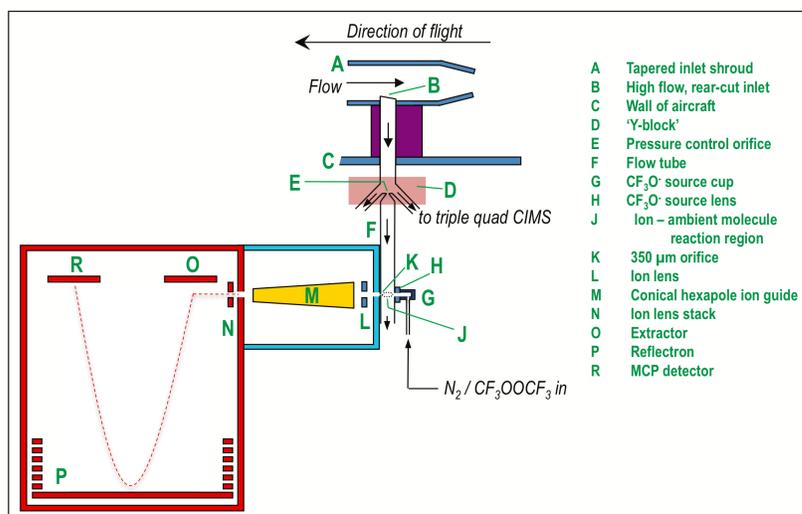


Figure 1. Schematic of refurbished Caltech S-CIMS with ToF mass analyzer.

and simultaneous data products from the S-CIMS instrument for all mass channels [Drewnick *et al.*, 2005].

We have flown a tandem CIMS (T-CIMS) instrument in addition to the S-CIMS since INTEX-B (2006). A schematic of this instrument is shown in Figure 2.

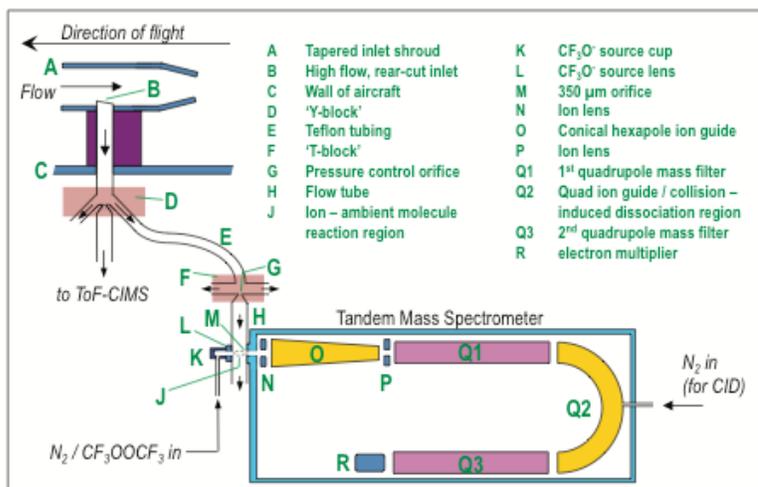


Figure 2. Schematic of Caltech T-CIMS. Q1 is used to select 'parent ions' for the target analyte (e.g., CH₃OOH·CF₃O⁺). Ions selected in Q1 pass into the Q2 ion guide, where they are dissociated by collisions with N₂. The second mass filter quadrupole (Q3) is used to select the dissociation product ions (e.g. CF₃O⁺) [St. Clair et al., 2010].

The T-CIMS provides parent-daughter mass analysis, enabling measurement of compounds precluded from quantification by the S-CIMS due to mass interferences (e.g. MHP) or the presence of isobaric compounds (e.g. isoprene oxidation products) [Paulot et al., 2009b; St. Clair et al., 2010].

Calibrations of both CIMS instruments for HNO₃ and organic acids are performed in flight using

isotopically-labeled reagents evolved from a thermally-stabilized permeation tube oven [Washenfelder et al., 2003]. By using an isotopically labeled standard, the product ion signals are distinct from the natural analyte and calibration can be performed at any time without adversely affecting the ambient measurement. We also fly calibration standards for H₂O₂ (evolved from urea-hydrogen peroxide) and MHP (from a diffusion vial).

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