On the ionization mechanism in atmospheric pressure negative ion mass spectrometry – the role of ozone and CO_2 –

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Introduction

Background:

- The ionization mechanisms prevailing in negative ion atmospheric pressure mass spectrometry are not yet fully unraveled
- Determination of the influence of different reagent ions on the ionization mechanism and analyte ion product distribution is necessary
- Different ionization methods, e.g., APPI, APCI, DART or electron generation via the photoelectric effect (APECI) appear to exhibit largely identical ionization mechanisms following reagent ion generation [11]
- Ionization methods such as APPI or APECI produce large amounts of ozone when oxygen is present in the irradiated ion source region
- Small molecules, which are ubiquitous in atmospheric pressure ion sources (e.g., CO_2) or generated during the ionization process (e.g., O_3 or NO_3) may influence the ionization process
- Rate constants of reactions regarding these molecules and their ions are well known from e.g. atmospheric chemistry
- The reaction time, i.e., the dwell time in the collision dominated regions of the sampling stages of the mass spectrometer seems to be a crucial factor determining the primary ion distribution

Approach:

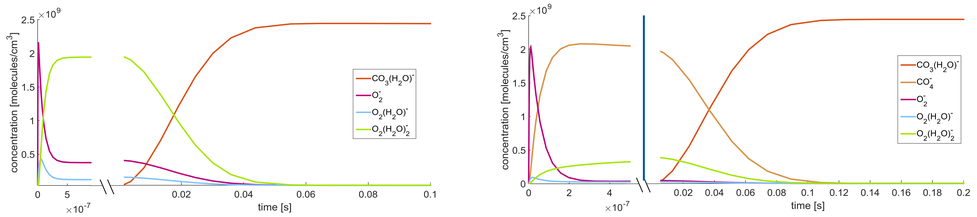
- Using APPI and APECI with different transfer times
- Kinetic simulations are used to reproduce the experimental results
- The applied reaction scheme includes 152 reactions. The rate constants are taken from [1-8]

Kinetic Simulations of the Reactant Ion Population

Short Photolysis and Reaction Time

Using APECI, photolysis takes place during 400 µs at 185 nm, resulting in **270 pptV** ozone. With the VUV (APPI) lamp **1.8 ppbV** ozone are produced.

Synthetic Air — **APECI/APPI** — **Synthetic Air + 0.3 % CO_2**

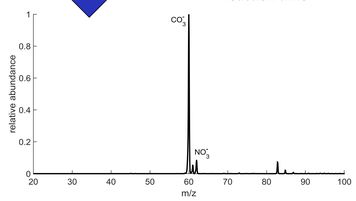


Above: In synthetic air, both ionization methods yield essentially similar reactant ion populations: Only O_2^- and $[O_2(H_2O)_n]^-$ reagent ions are observed after **1 ms** transfer time.

Equilibrium is reached after **50 ms**; in this case $[CO_3(H_2O)]^-$ is the only reactant ion present.

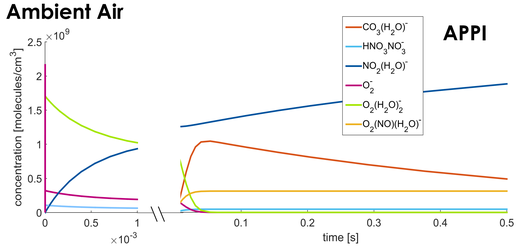
Right: Increasing the carbon dioxide concentration leads to a shift of the ion population from superoxide to CO_4^-. The mass spectrum recorded with APECI shows CO_3^- as most abundant ion, probably due to missing reactions in the kinetic reaction scheme regarding the CO_x^- - conversion reactions.

After **1 ms** reaction time



The same short photolysis time, but increased CO_2 and NO_2 mixing ratios, lead to a more diverse reactant ion population

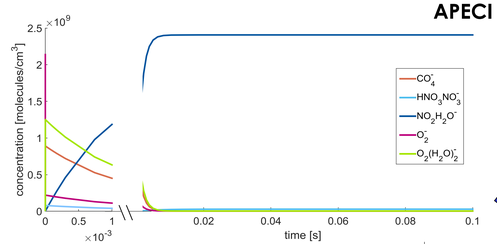
Ambient Air



APPI

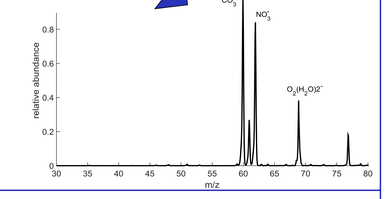
Left: The VUV lamp yields a higher ozone mixing ratio. In ambient air this results in a higher concentration of $[O_2(H_2O)_2]^-$ after **1 ms** than with less ozone present. In the equilibrium state $[CO_3(H_2O)]^-$ and $[O_2(NO)(H_2O)]^-$ are also present in addition to $[NO_2(H_2O)]^-$.

APECI



Left: With lower ozone mixing ratio, $[NO_2(H_2O)]^-$ is the only reactant ion after **10 ms**. After the transfer time (**1 ms**) equilibrium is not reached in the cAPECI ion source, thus superoxide water clusters and CO_4^- are present as reactant ions.

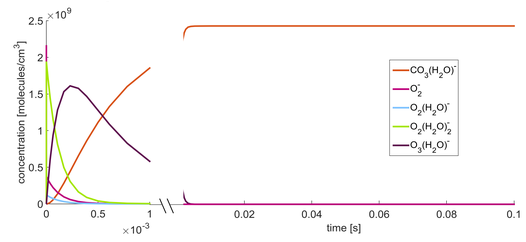
Right: The mass spectrum of APECI in ambient air with a reaction time of approx. **1 ms** reproduces the kinetic simulation.



Longer Photolysis and Reaction Time (1ppmV ozone)

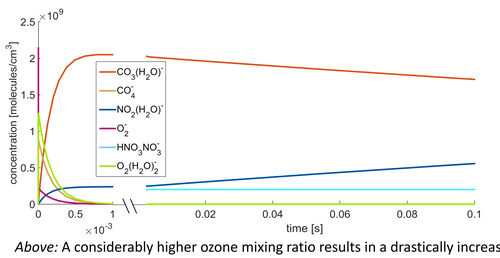
In both, synthetic air and ambient air, $[CO_3(H_2O)]^-$ is the most abundant reactant ion.

Synthetic Air

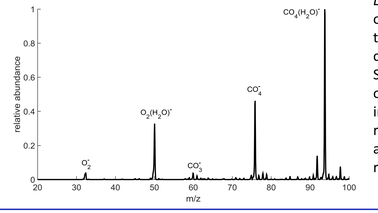


Above: A longer photolysis time results in higher ozone mixing ratio. An ozone mixing ratio of **1 ppmV** corresponds to a photolysis time of approx. **1.25 s** for the PenRay lamp and approx. **250 ms** for the VUV lamp.

Ambient Air



Above: A considerably higher ozone mixing ratio results in a drastically increased CO_3^- - water cluster concentration. The unreactive NO_x^- -population is significantly decreased compared with ionization methods using discharges, which in contrast increase the background NO_x concentration.



Left: In the APPI mass spectrum of ambient air with a reaction time of approx. 1 s CO_x^- (water clusters) are observed. Superoxide water clusters are observed instead of NO_x^-, indicating a lower NO_2 mixing ratio during the measurement as compared to the simulation result.

Conclusions

- The experimentally determined mass spectra are well reproduced by the kinetic simulations
- Small deviations are observed, most probably due to missing reactions in the reaction scheme
- For short photolysis times, as realized in the capillary APECI source, only small amounts of ozone are generated
- In synthetic air:
  - Superoxide water clusters are the only reactant ions observed after 1 ms, longer reaction times lead to CO_4^-
  - Increasing the carbon dioxide concentration leads to a shift in the reactant ion population towards CO_4^- in the simulation toward CO_3^- in the experiments
- In ambient air the amount of ozone produced controls the reactant ion population
  - Low ozone mixing ratios (APECI) lead to NO_x^--ions after long reaction times, which are unreactive towards most analytes. Short reaction times allow that superoxide is present as reactive species
  - High ozone mixing ratios (APPI) lead to a higher amount of CO_x^-, which is more reactive than NO_x^-
- Short reaction times (capillary ion source) and/or the absence of neutral photolysis products (APLI) are beneficial to obtain favorable reactant ion populations consisting solely of superoxide and CO_x^-

Literature

1) F.C.Fehsenfeld, A.L.Schmeltekopf, H.I.Schiff, E.E.Ferguson; *Laboratory Measurements of negative ion reactions of atmospheric interest*, Planet Space Sci., 15, 1967
2) B.Gravendeel, F.J.de Hoog; *Clustered negative ions in atmospheric negative corona discharges in the Trichel regime*, J. Phys. B.: At. Mol. Phys., 20, 1987
3) F.C.Fehsenfeld, E.E.Ferguson; *Laboratory studies of negative ion reactions with atmospheric trace constituents*, J. Chem. Phys., 61, 1974
4) D.W.Fahey, H.Böhringer, F.C.Fehsenfeld, E.E.Ferguson; *Reaction rate constants for O2-(H2O)n ions n = 0 to 4, with O3, NO, SO2, CO2*, J. Chem. Phys., 76(4), 1982
5) R.G. Ewing, M.J.Waltman; *Mechanisms for negative reactant ion formation in an atmospheric pressure corona discharge*, Int. J. Ion Mobil. Spec., 12, 2009
6) E.E.Ferguson; *Negative ion – molecule reactions,* Can. J. Chem., 47, 1969
7) J.D.Skalny, T.Mikovíny, S.Matejcik, N.J.Mason; *An analysis of mass spectrometric study of negative ions extracted from negative corona discharge in air,* Int. J. Mass Spec., 233, 2004
8) K.Naguto, Y.Matsui, T.Miyata, T.Yamauchi; *An analysis of the evolution of negative ions produced by a corona ionizer in air,* Int. J. Mass Spec., 248, 2006
9) V.Derpmann, S.Albrecht, T.Benter; *The Role of Ion Bound Cluster Formation in Negative Ion Mass Spectrometry*, Rapid Comm. Mass Spectrom. 26, 2012
10) V. Derpmann, W. Wissdorf, D. Mueller, T. Benter; *Development of a New Ion Source for Capillary Atmospheric Pressure Electron Capture Ionization*, 60th ASMS Conference on Mass Spectrometry and Allied Topics Vancouver, BC, Canada, 2012
11) C.N.McEwen, B.S.Larsen; *Ionization mechanisms related to negative ion APPI, APCI and DART, J. Am.* Soc. Mass Spectrom., 20, 2009

Methods

Experimental Setup

MS:	Esquire 6000 QIT, Bruker Daltonic
APPI:	Kr-RF-VUV lamp, λ=124 nm
APECI:	Low pressure mercury lamp (PenRay) λ=185 nm, anodized aluminum as photoemissive material
APLI:	CryLas FQSS 266-50 Nd:YAG; λ= 266 nm
Ion Sources:	Custom-built capillary ion sources with approx. 400 µs or 1 s photolysis transfer time
Ozone Detector:	Environment S.A. O3 42 Module
Kinetic analysis:	Chemked reaction kinetics solver, Version 3.3

Simulation Parameters

Start Concentrations

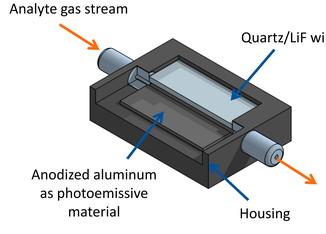
	Concentrations Synth. Air	S. Air + CO_2	Ambient Air
N_2	80 %	80 %	79 %
O_2	20 %	20 %	20 %
H_2O	100 ppmV	100 ppmV	1 %
NO	0.1 ppbV	0.1 ppbV	5 ppbV
NO_2	0.1 ppbV	0.1 ppbV	50 ppbV
HNO_3	10 pptV	10 pptV	10 pptV
CO_2	0.1 ppmV	0.3 %	0.04 %
electrons	100 pptV	100 pptV	100 pptV
O_3	Determined by photolysis time and measurements; concentrations given above		

Possible Reactant Ions

O^-, $O(H_2O)^-$, O_2^-, O_4^-, $O_2(H_2O)^-$, $O_2(H_2O)_2^-$, $O_2(H_2O)_3^-$, $O_2(H_2O)_4^-$, O_3^-, $O_3(H_2O)^-$, $O_3(H_2O)_2^-$, $O_3(H_2O)_3^-$, OH^-, $OH(H_2O)^-$, $OH(H_2O)_2^-$, CO_3^-, $CO_3(H_2O)^-$, CO_4^-, HCO_3^-, $HCO_3(H_2O)^-$, N_2O^-, NO_2^-, $NO_2(H_2O)^-$, $HNO_3NO_3^-$, NO_3^-, $O_2NO(H_2O)^-$, $O_2NO(H_2O)_2^-$

Ion Source

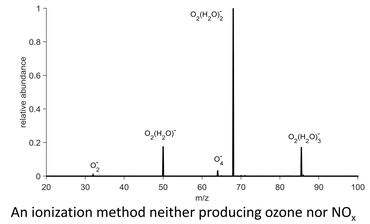
Short Photolysis and Reaction Time



Photolysis time: approx. 400 µs; Transfer time: approx. 1 ms

Ionization takes place in an ion source integrated into an inlet capillary. A UV- or VUV-lamp mounted on top of the ion source provides the light for photoelectron generation (APECI) or for single photon generation (APPI). A flute milled inside the metal leads to an identical gas flow as compared to standard capillaries. The photoemissive material is anodized aluminum.

DA-APLI



An ionization method neither producing ozone nor NO_x through photolysis is dopant assisted atmospheric pressure laser ionization. Thus exclusively superoxide water clusters are generated as reactant ions, even in ambient air.

Acknowledgement

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