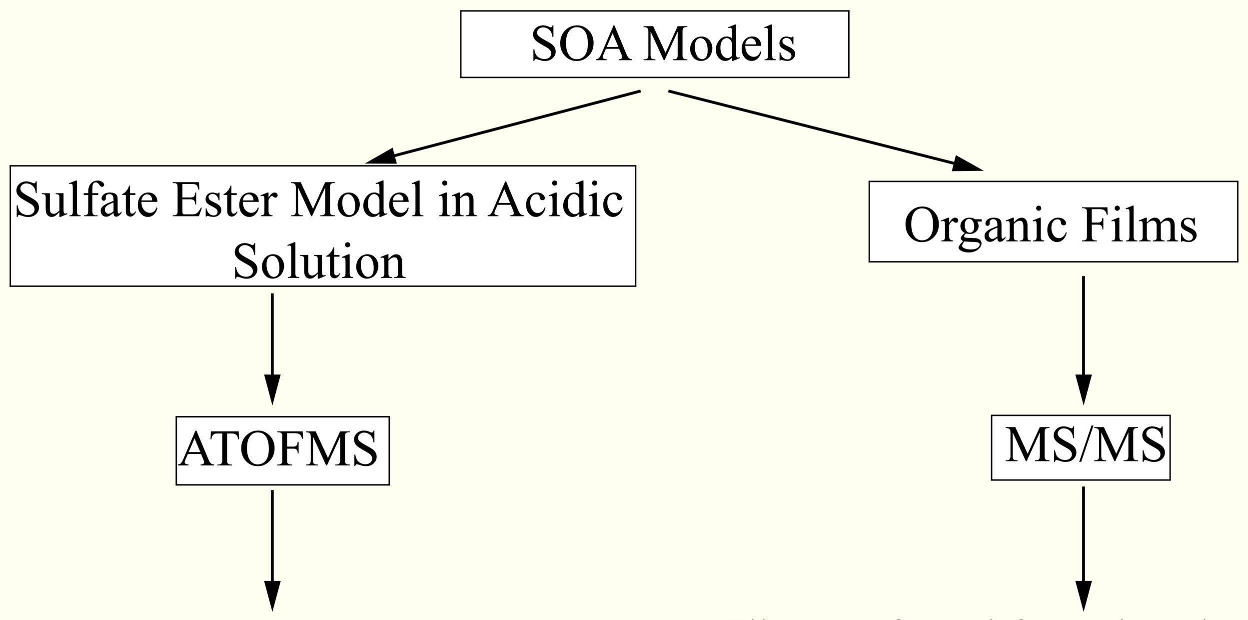
Mass Spectrometry for the Analysis of SOA Model Compounds

Ross Hamilton (1), Keven Tell (1), Deborah Gross (1), Annalise Van Wyngarden (2), Laura Iraci (2)

1) Department of Chemistry, Carleton College, Northfield, MN 55057 2) NASA Ames Research Center, Moffett Fld Mountain View, CA 94040

INTRODUCTION

Secondary organic aerosols (SOA) are of increasing importance in the atmosphere. The formation of SOA is often acid catalyzed, and since sulfuric acid is readily formed in the atmosphere, it is important to study the types of compounds that can be formed under acidic conditions and how well we can measure and identify these compounds. We are taking two approaches to investigate compounds of this type using mass spectrometry.



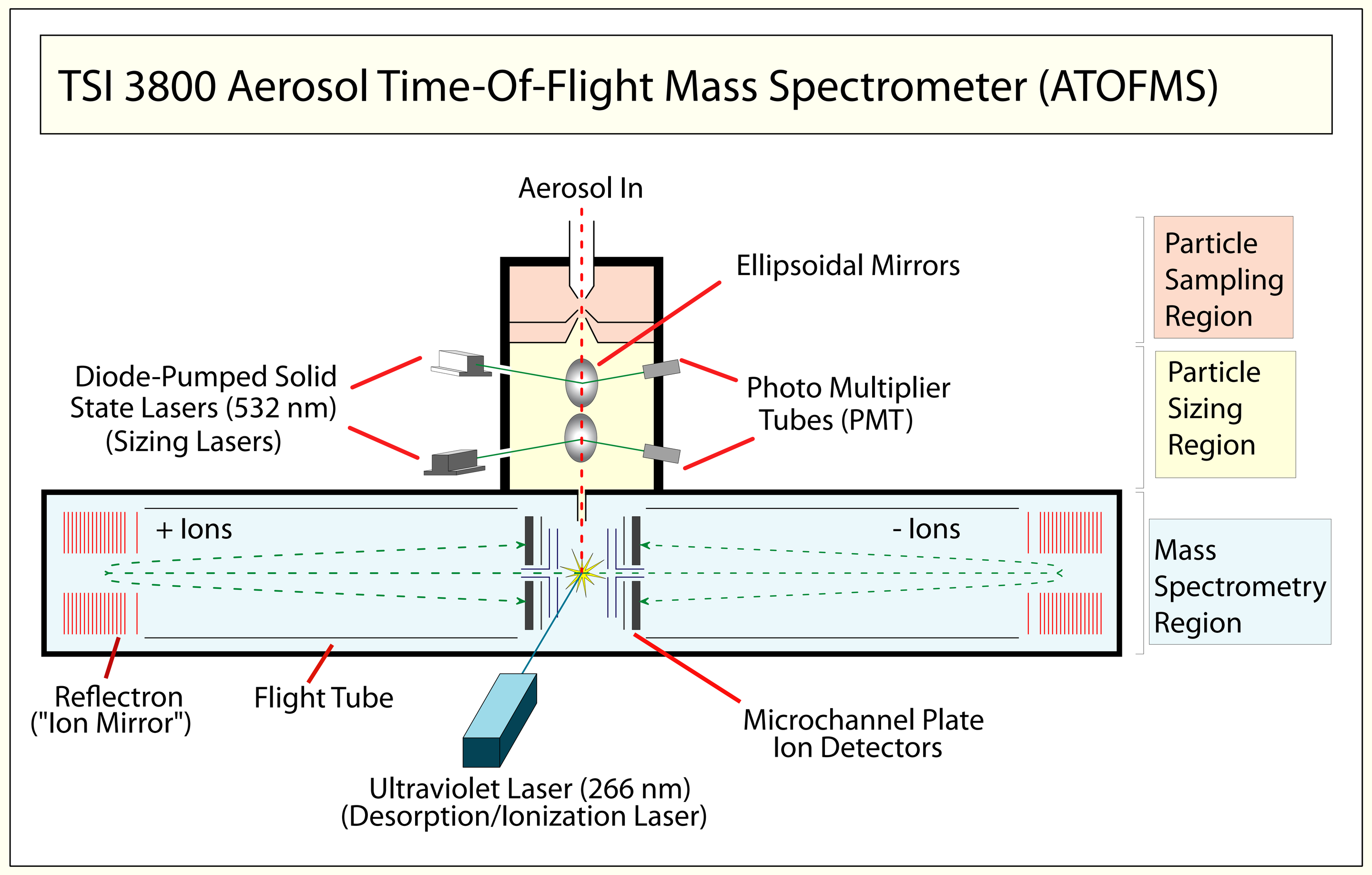
In order to understand how the ATOFMS signal depends on the composition and acidity of SOA particles, known particle types are analyzed under real-world conditions. We focus on sulfate esters, one chemical component of SOA that has been proposed to form by acid-catalysis, and show that the ion signal from the molecular ion is dramatically enhanced in acidic solutions.

Films are formed from glyoxal and propanal in high concentrations of sulfuric acid in bulk solution. The opaque films formed could have an impact on the optical properties of the particles and their ability to take up water. The composition of the reaction products is investigated using MS/MS experiments, through which we are trying to identify the high-mass species (up to ~650 amu) present in the mass spectra.

METHODS

The organic films studied here were made by mixing 78% by weight sulfuric acid with propanal and glyoxal. The solution immediately turned dark brown and a solid film formed on the surface. A 1 to 200 dilution of the solution was made before it was directly infused into the ESI source of a Thermo LCQ Duo Mass Spectrometer. MS and tandem mass spectrometry were used to identify the components of this solution.

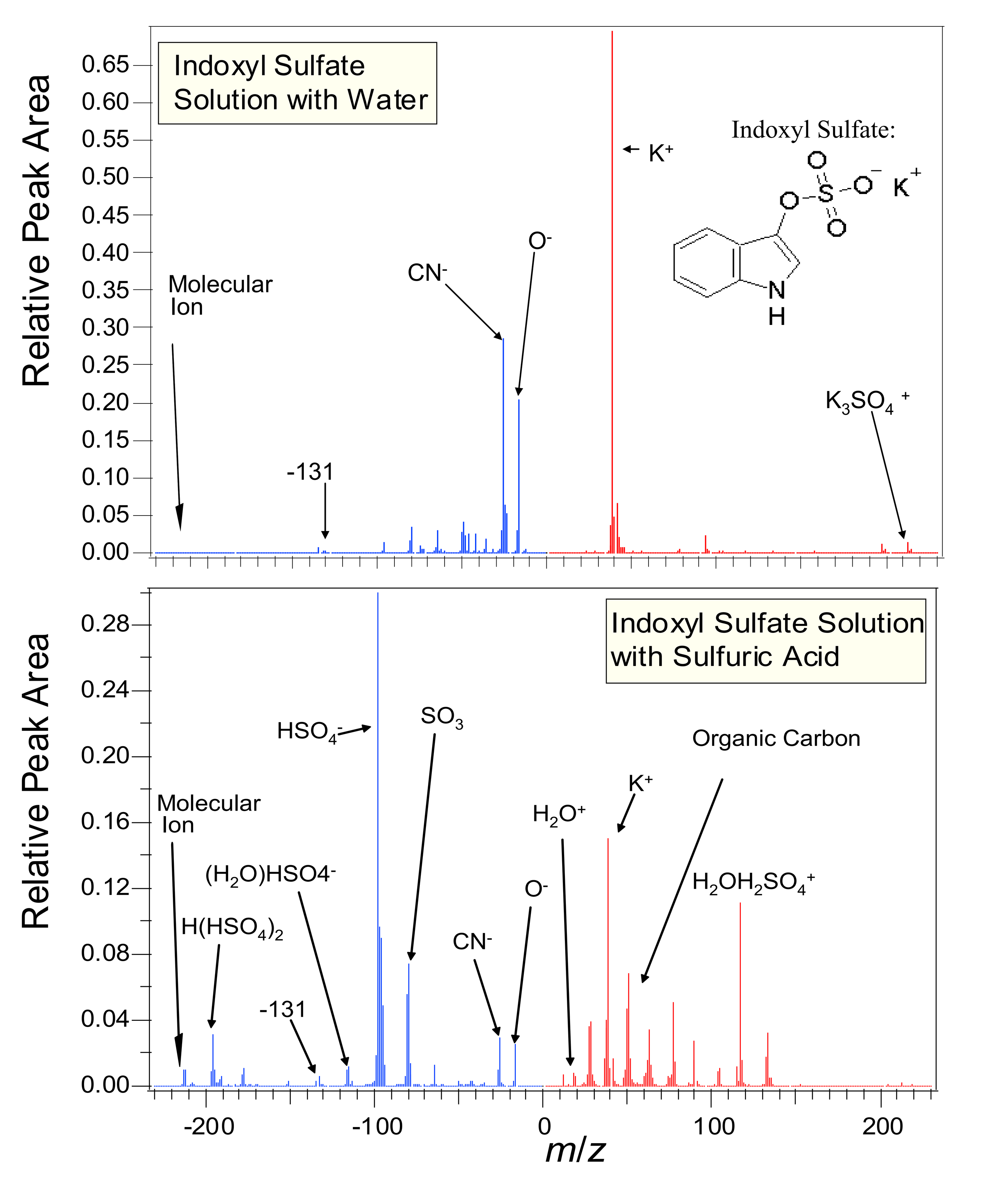
The TSI 3800 ATOFMS is a single particle aerosol mass spectrometer. The ATOFMS will determine the particle's velocity, which can be calibrated to vacuum aerodynamic diameter. The ionization laser (4th harmonic of a pulsed Nd:YAG, 266 nm) fires at the particle and ionizes it in the source region. Ions travel through the time-of-flight mass spectrometers (one for each ion polatiry), and are detected by microchannel plate detectors, generating two mass spectra per particle. Particles were generated using a TSI nebulizer.



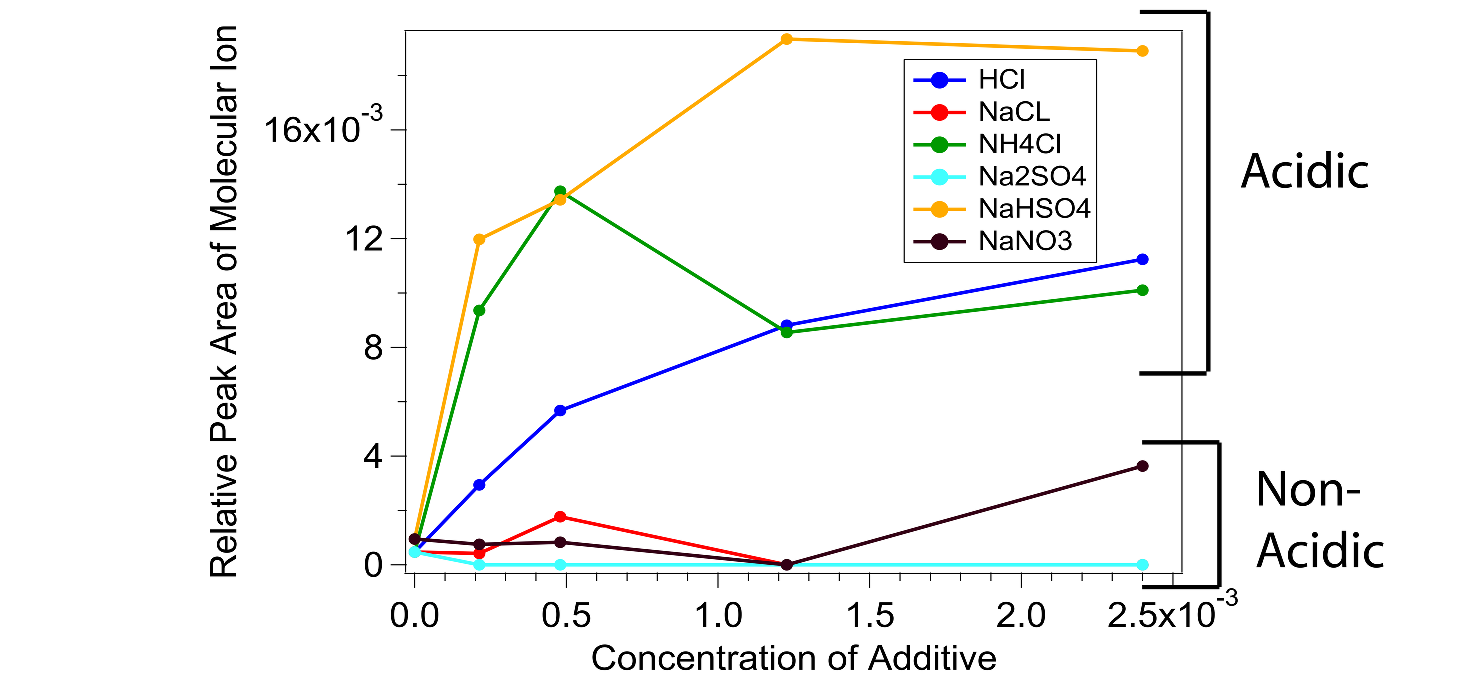
RESULTS

ATOFMS for Sulfate Ester Model

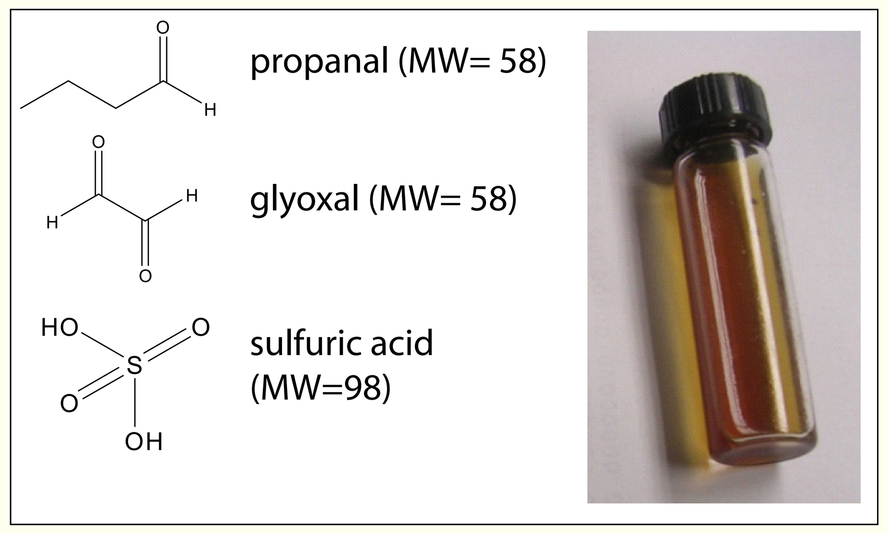
The top graph shows the average single-particle mass spectrum determined from particles nebulized from a solution of indoxyl sulfate. Note that the molecule is a potassium salt, explaining the high intensity potassium ion. A very low intensity peak is observed for the pseudo-molecular ion in the negative ion mass spectrum. The lower figure shows the results when a solution of the same concentration of indoxyl sulfate is mixed with a low concentration of sulfuric acid and then nebulized. Note that the relative peak area of the molecular ion increases, and other peaks (especially due to sulfate) are seen.



The graph below summarizes the results of all indoxyl sulfate and additive solutions we tested. Note that acidic additives generate a higher relative peak area for the molecular ion peak, while the non-acidic additives have essentially no effect.

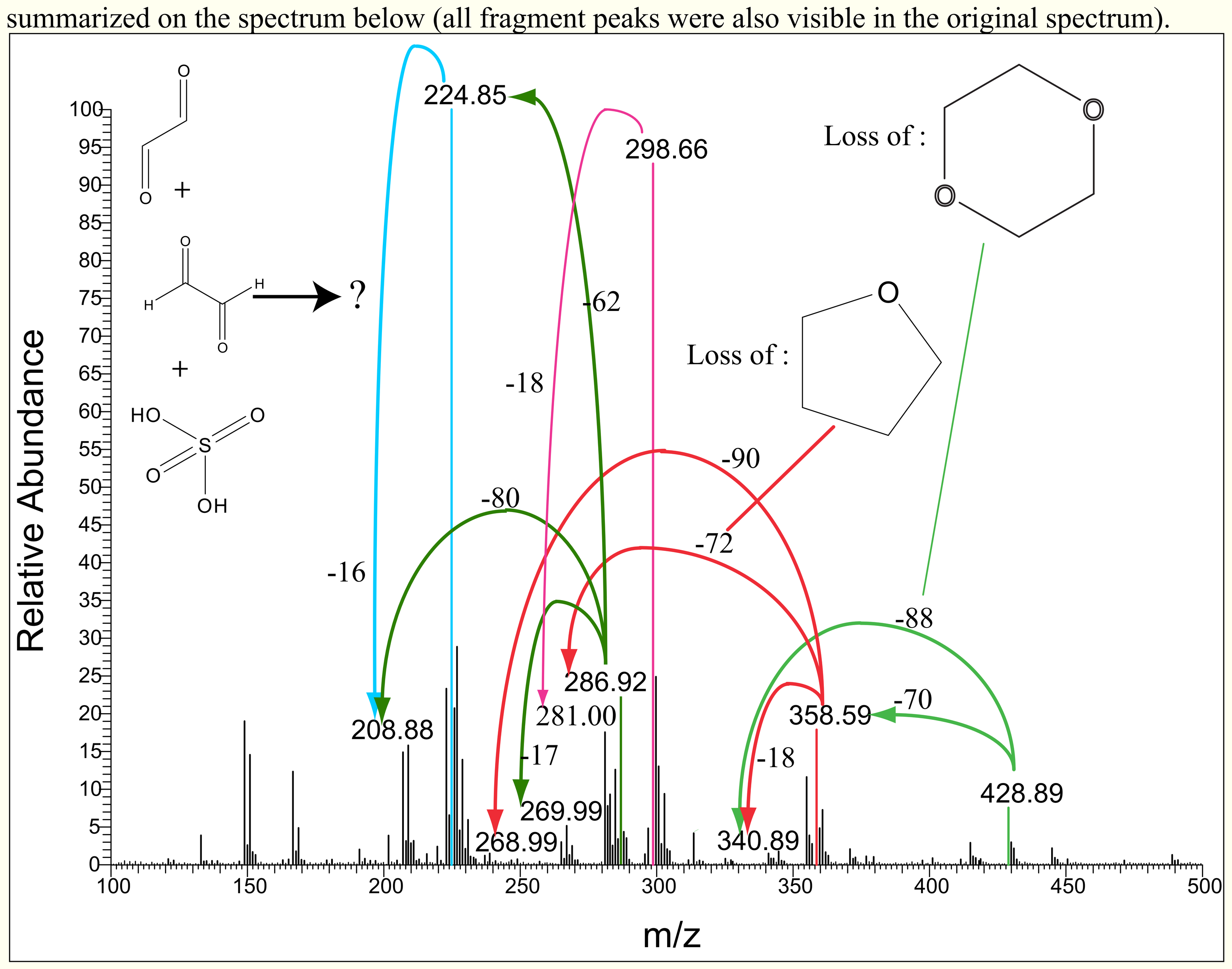


Organic Films



A solution of 0.03 M glyoxal, a solution of 0.03 M propanal in 78% by weight sulfuric acid (all clear solutions) were mixed to create the solutions shown at the right. This forms its dark brown film immediately after the precursor solutions are mixed together. Some other combinations of these precursors also form films over various time scales, from days to weeks.

The following graph shows the average mass spectrum obtained using ESI-MS for analysis of the solutions formed above, diluted 1:200 in water. After obtaining this spectrum, a series of MS/MS experiments were run using the same solution. The precursor peak of each MS/MS experiment is designated by a different color, and lines are drawn to the fragment peaks using the same colored lines, summarized on the spectrum below (all fragment peaks were also visible in the original spectrum).



Some of the precursor peaks fragment in ways that give similar fragments to other parent peaks. This information is useful in determining the composition and structure of the products of this reaction. Five peaks were used as precursors for MS/MS experiments: *m/z* 428, *m/z* 358, *m/z* 298, *m/z* 286, and *m/z* 224. Notice how many of the precursors break apart to form similar fragments in the MS/MS experiments. For example, both *m/z* 286 and *m/z* 224 break apart to form a 208 *m/z* fragment during MS/MS experiments. Also included on the spectrum are some proposed structures that correspond to significant fragments.

CONCLUSIONS AND FUTURE WORK

The composition and acidity of SOA particles does affect the ATOFMS signal. It appears that an increase in acidity will yield an increase in the signal of the molecular ion, while an increase in the concentration of additive alone doesn't. While the composition of the organic film solution has not been fully identified, important steps have been made in analyzing and understanding them. More work needs to be done to identify this organic film solution. Performing more MS/MS experiments will give more information about the components of the film and will be important in identifying the components as well as the structure of the organic film solution.

Acknowledgements:

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