

FUNDAMENTAL STUDIES OF THE MECHANISMS
AND APPLICATIONS OF FIELD-INDUCED
DROPLET IONIZATION MASS SPECTROMETRY
AND ELECTROSPRAY MASS SPECTROMETRY

Thesis by

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In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2006

(Defended August 25, 2005)

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Acknowledgements

I thank everyone. That's right. Everyone.

Abstract

This thesis explores the evaporation and Rayleigh discharge dynamics of highly charged micron-sized droplets and explores new methodologies for extracting ions for mass analysis from neutral droplets using strong electric fields in a technique termed field-induced droplet ionization.

A phase Doppler anemometer characterizes individual highly charged droplets moving through a uniform, mild electric field within an ion mobility cell according to size, velocity, and charge. Repeated reversals of the electric field allow multiple characterizations on selected droplets. This “ping-pong” technique provides droplet histories that determine the solvent evaporation and Rayleigh discharge behavior. The ping-pong experiment characterizes volatile droplets of the hydrocarbon solvents *n*-heptane, *n*-octane, and *p*-xylene as well as two-component droplets of either 2-methoxyethanol, *tert*-butanol, or *m*-nitrobenzyl alcohol with methanol. On average, hydrocarbon droplets eject 18% of their net charge into progeny droplets with an undetectable loss in mass. Rayleigh discharge events in the polar, binary droplets release between 20 and 35% of the net charge with a correspondingly undetectable loss in mass.

In other experiments, strong electric fields elongate neutral droplets along the field axis. Field-induced droplet ionization (FIDI) occurs at sufficient field strengths as the droplets eject opposing jets of positively and negatively charged progeny droplets. Images of droplets from a vibrating orifice aerosol generator illustrate this phenomenon, and mass spectrometric sampling of the progeny droplets demonstrates that they are a viable source of desolvated gas-phase ions. Switched electric field experiments relate the timescale of droplet elongation and progeny droplet formation in FIDI to the timescale of oscillations of droplets in sub-critical field strengths. FIDI mass spectra are presented for several species, including tetraheptyl ammonium cation, deprotonated benzene tetracarboxylic acid, and multiply protonated cytochrome *c*.

Droplets may serve as reactors before being sampled by FIDI-MS. FIDI-MS probes the products of heterogeneous reactions between solution-phase oleic acid or a lysophosphatidic acid and gas-phase ozone.

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List of Abbreviations and Terms

- EDB electrodynamic balance
- ESI electrospray ionization
- FIDI field-induced droplet ionization
- ICR ion cyclotron resonance
(Typically used in conjunction with MS, i.e. ICR-MS)
- IMS ion mobility spectrometer (instrument context)
or ion mobility spectrometry (technique context)
- LCQ An ion trap mass spectrometer employed by the Beauchamp group
- MS mass spectrometer (instrument context)
or mass spectrometry (technique context)
- PDA phase Doppler anemometer (instrument context)
or phase Doppler anemometry (technique context)
- LPA lysophosphatidic acid
Lysophosphatidic acid is a general term for a class of compounds having a similar formula and biological role. This thesis only considers oleoyl-L- α -lysophosphatidic acid.

