# Nanosecond Pulse Ionization Wave Discharges on Liquid Surfaces: Discharge Development and Plasma Chemistry

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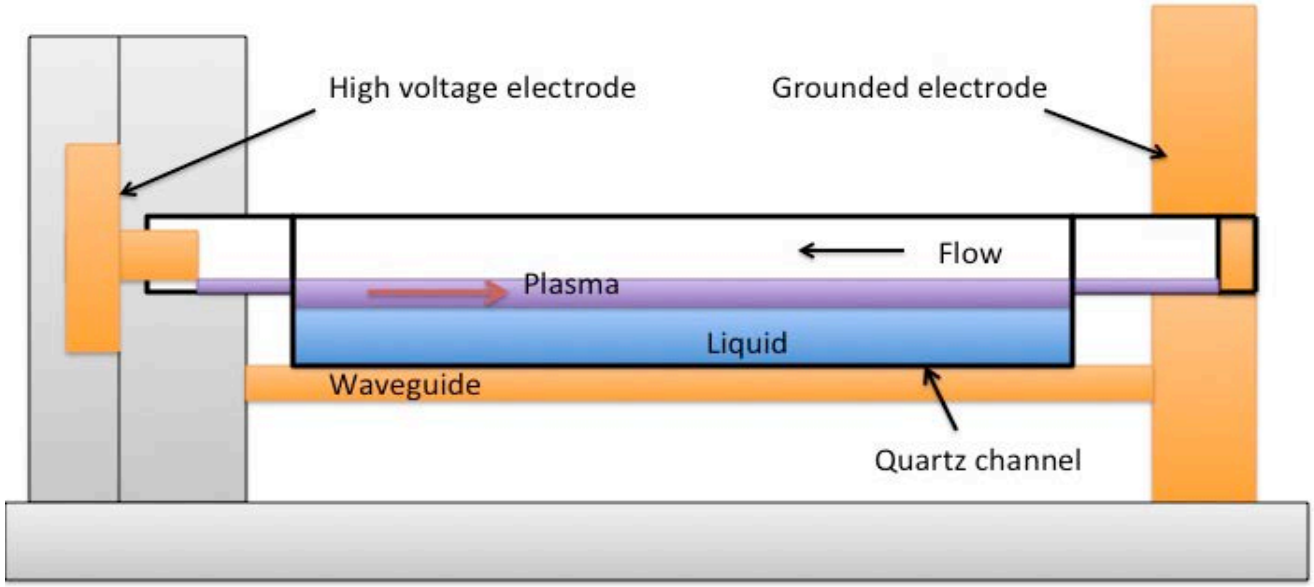
# Ionization waves at liquid-vapor interface: Why are we interested?

- Previous work: surface ionization wave, diffuse "sheet" plasmas in nitrogen and air over a solid dielectric (quartz): propagate over tens of cm, wave speed ~ 0.1 cm/ns for dU/dt~ 0.1 kV/ns
- Produced by high voltage, ns duration pulses, with very good shot-to-shot reproducibility: potential for quantitative studies of near-surface plasma kinetics using optical diagnostics
- Reproducible wave generation over liquid dielectrics (water, aqueous solutions, alcohols, liquid hydrocarbons): should also be possible, liquid surface distortion, induced flow appear unlikely due to short pulse duration (~100 ns)
- Caution: long-term surface charge accumulation may still induce liquid surface perturbation, flow on a long time scale, and may well be a critical issue
- Significant electric field enhancement near liquid surface ($\varepsilon_{water}$ ~ 80): high energy threshold electron impact processes (dissociation and ionization) may become very efficient
- Near room temperature plasma at high energy loading: Joule heating balanced by evaporative cooling of liquid (heat of vaporization ~ 0.4 eV/molecule), high specific heat of liquid
- At high buffer gas flow rates, evaporation rate may be very high: potential for high-yield, near-surface plasma chemistry of evaporating reactants

# Ionization waves at liquid-vapor interface: What are we trying to do?

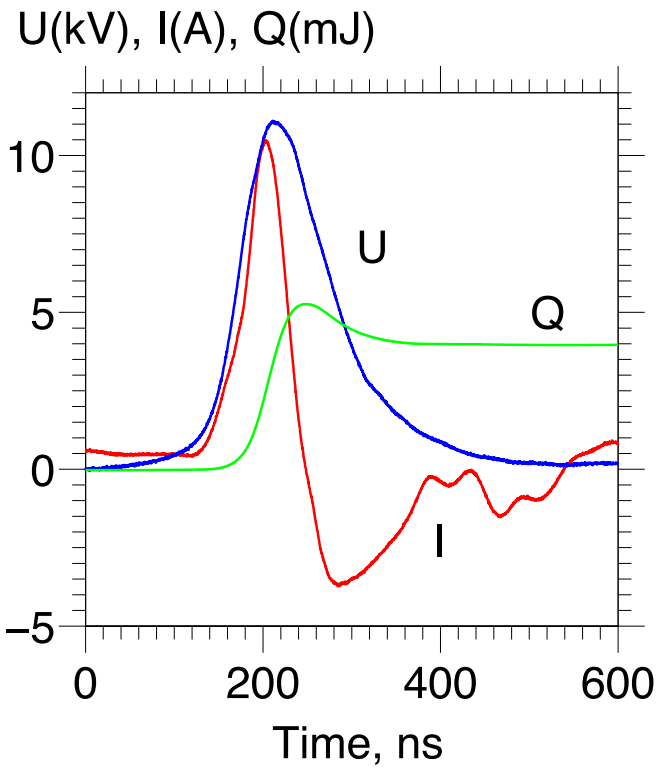
- **Determine range of conditions where nsec pulse, diffuse, reproducible surface ionization wave discharges propagate along liquid-vapor interfaces**
- **Characterize surface ionization wave dynamics, gain insight into dominant processes controlling wave propagation**
- **Demonstrate potential of this approach for studies of near-surface plasma chemistry, in particular electron impact processes generating reactive radical species from evaporating liquid reactants**
- **Use this approach for *in situ* measurements of time-resolved, absolute, 2-D distributions radical species concentrations (OH, H, O, NO, N) and temperature, by single-photon and two-photon absorption LIF, and Rayleigh scattering**
- **Use this approach for *ex situ* measurements of stable species concentrations ($NO_x$, hydrocarbons, and oxygenates), by FTIR absorption spectroscopy**
- **Use these data, as well as kinetic modeling, to determine kinetic mechanism of near-surface plasma chemical reactions**

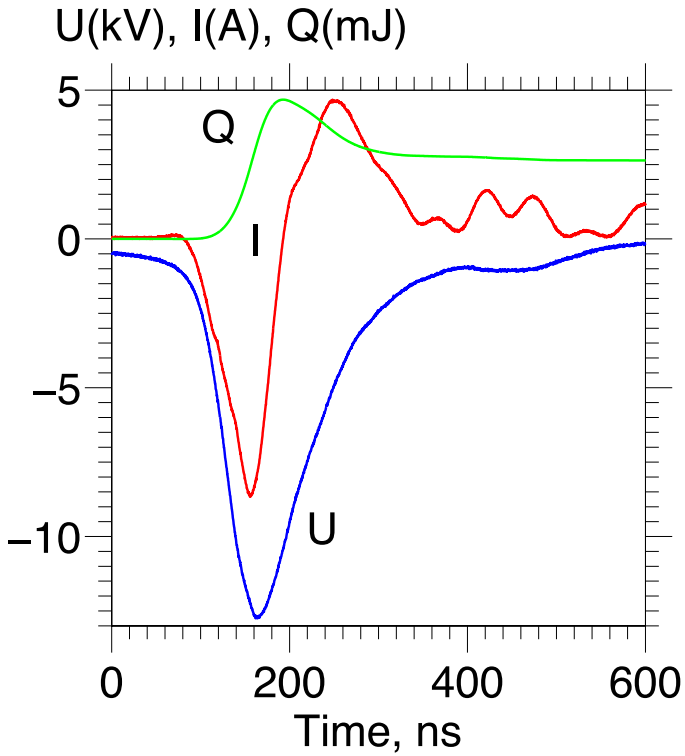
# Surface ionization wave discharge cell schematic




- Rectangular quartz channel, 25 mm side, 35 mm height, wall thickness 1.75 mm, 22 cm long, distance between electrodes 28 cm
- Grounded waveguide attached to bottom wall
- Liquid layer depth ≈ 5 mm, liquids used: distilled water, saline solution, 1-butanol
- Buffer gas flow ~ 10 cm/s (flow residence time ~1 s), typically nitrogen at P=10-20 torr
- High-voltage pulses: peak voltage ~10-15 kV, pulse duration ~ 100 ns, alternating polarity, pulse rep rate ~100 Hz
- Surface ionization wave, “sheet” plasma sustained over quartz wall or liquid-vapor interface
- Wave propagation monitored by a capacitive probe and ICCD imaging

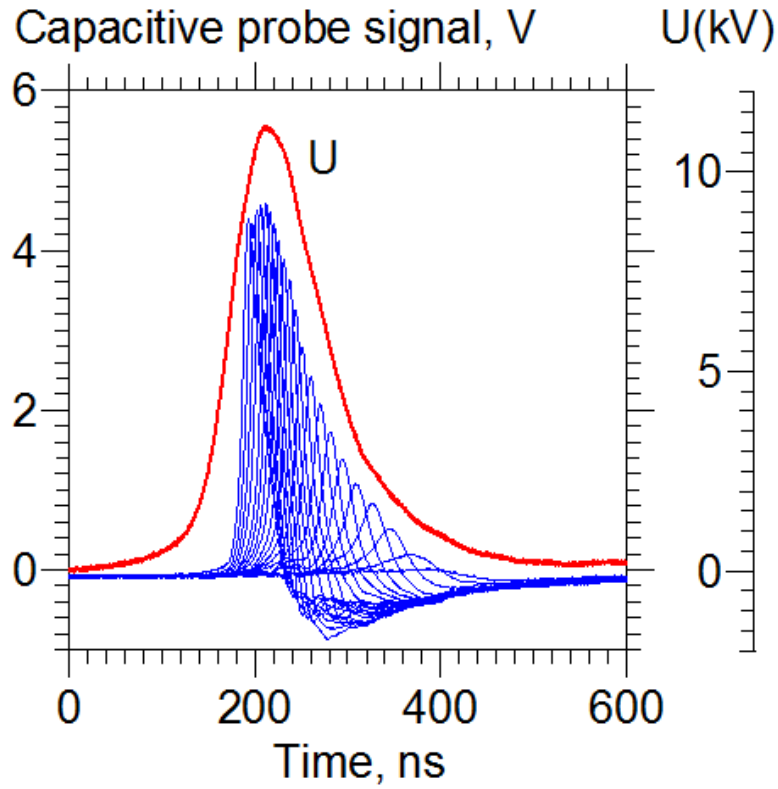
# Typical pulse waveforms

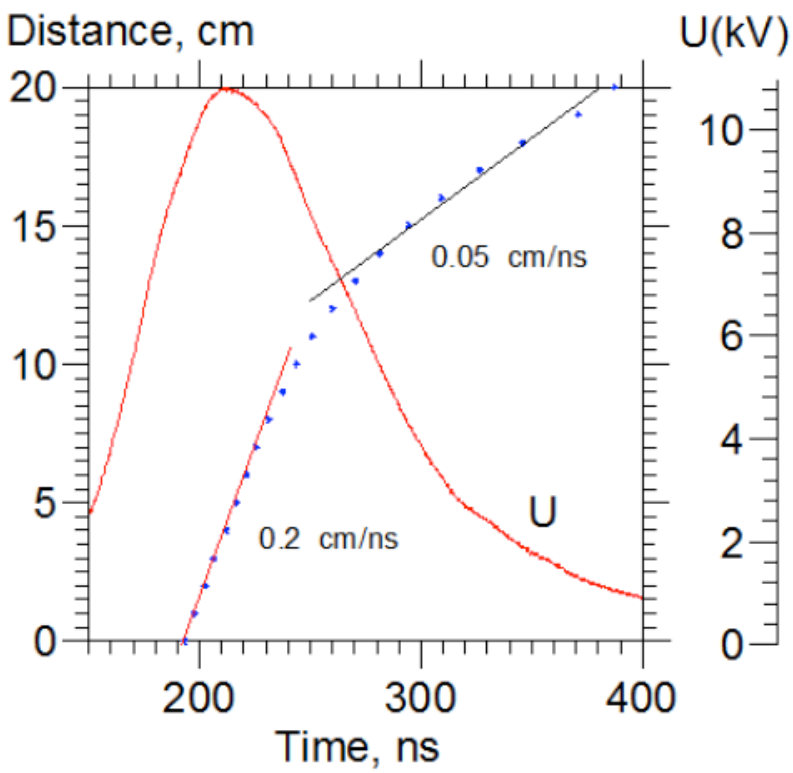



- **Pulse generator: alternating polarity waveform ( + / - )**
- **Positive or negative polarity pulses may be blocked using high-voltage diodes**
- **Waveforms shown for $N_2$ buffer, P=20 Torr, flow rate 0.2 SLM, positive and negative pulse polarities, wave over solid dielectric (quartz)**
- **Typical pulse coupled energy ~ 3-4 mJ/pulse**
- **Low pulse jitter, ~ 1-2 nsec**
- **Long pulse duration (~100 nsec) helps the wave reach the grounded electrode, establish direct current path, if desired**

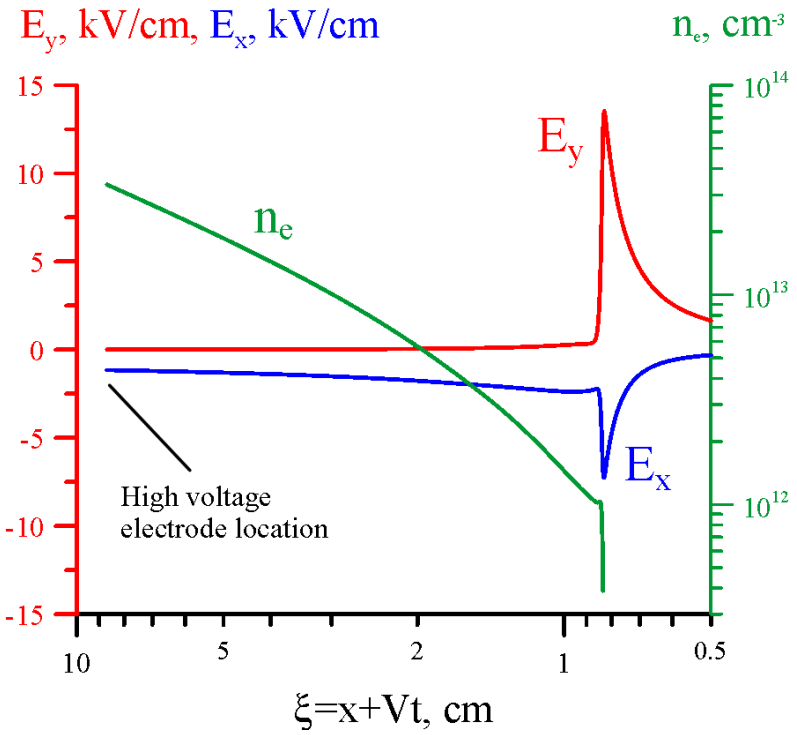
# Capacitive probe signal and wave *x-t* trajectory

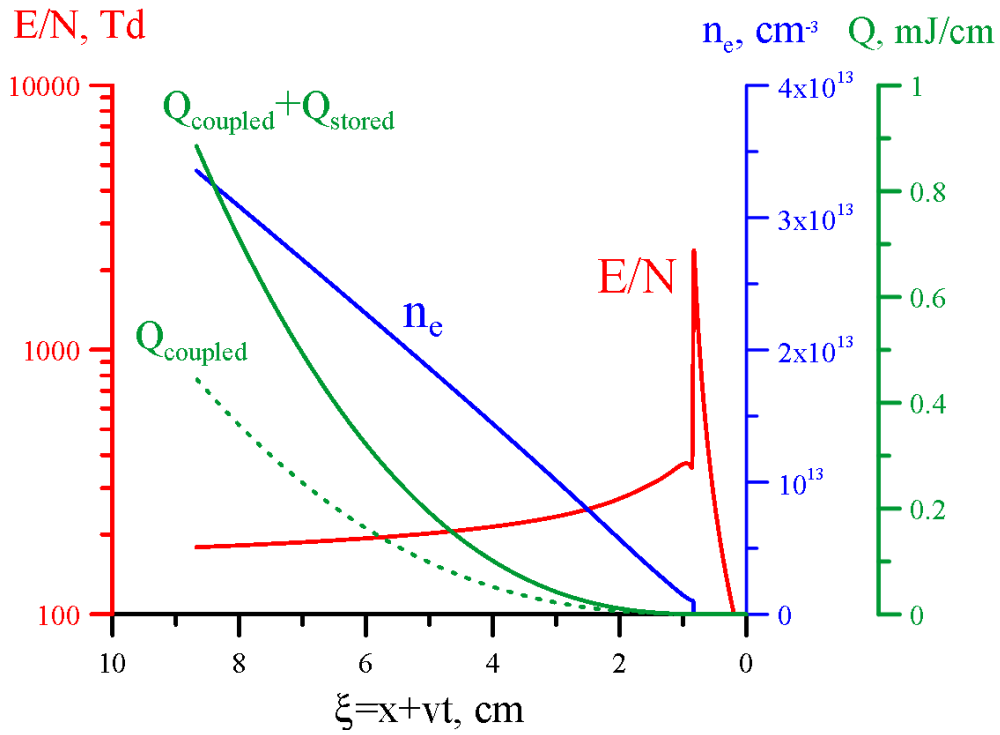



- Capacitive voltage divider probe can slide along the discharge channel, measures charged dielectric surface potential
- Waveforms shown for $N_2$ buffer, P=20 Torr, flow rate 0.2 SLM, positive pulse polarity, wave over solid dielectric (quartz)
- Wave speed gradually decreases from $V \approx 0.2$ cm/ns to $V \approx 0.05$ cm/ns, over $L \approx 20$ cm, as the pulse voltage decreases

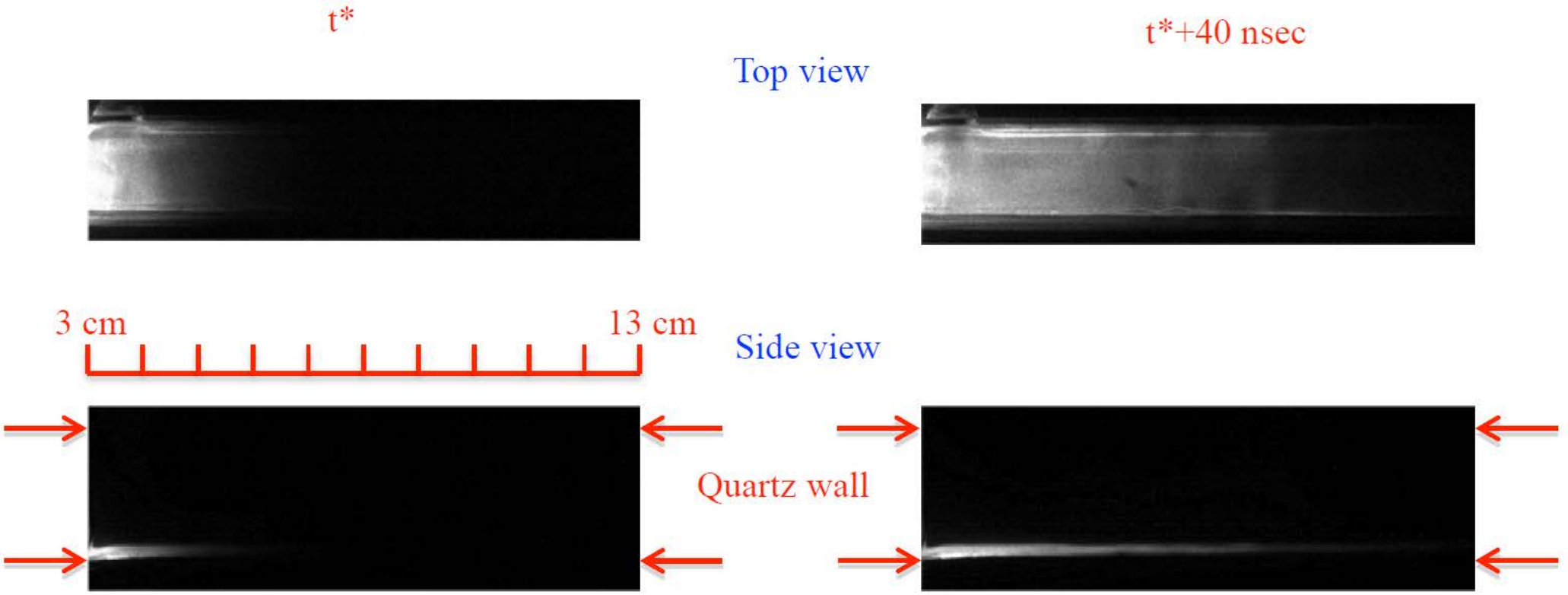
# Analytic solution for a negative polarity surface ionization wave over quartz: estimate of plasma parameters



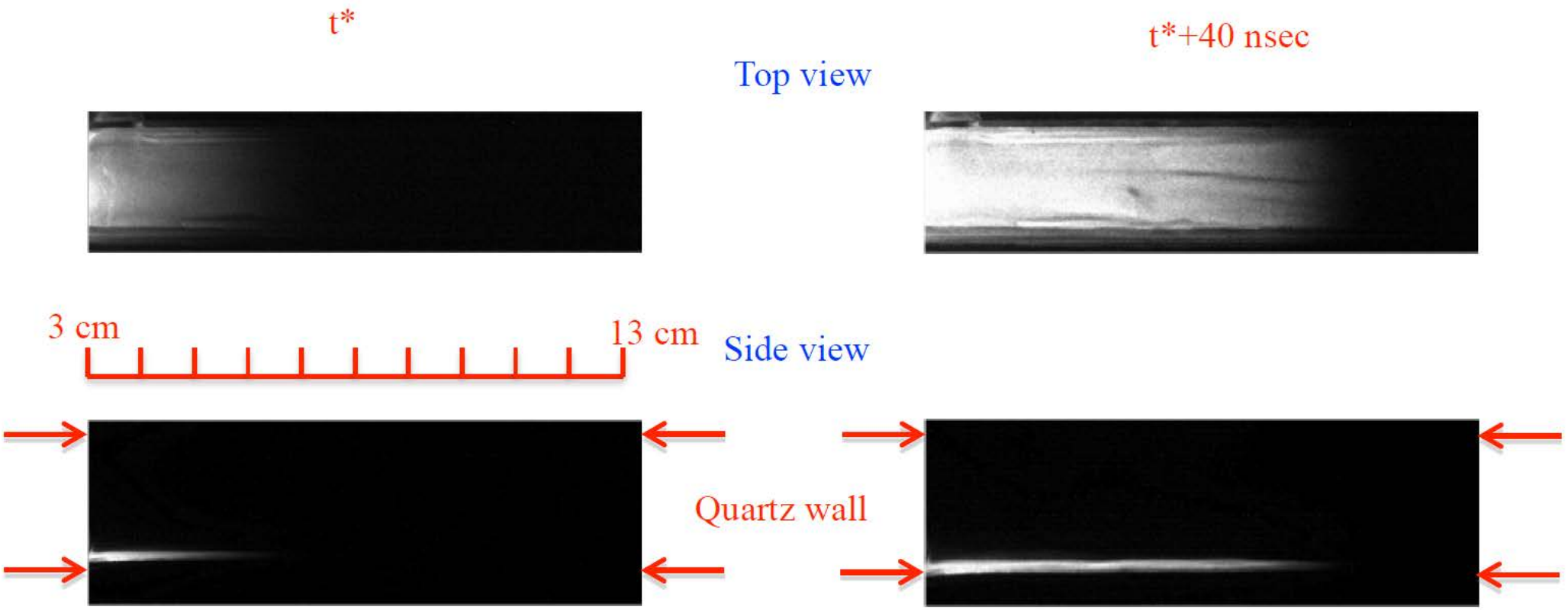

- **Self-similar solution: distributions "slide over" to the right at the wave speed, $V$**
- **Distributions of plasma parameters along a negative polarity surface ionization wave in nitrogen over quartz surface, for $P$ = 20 Torr, $dU/dt$ = 0.2 kV/ns**
- **Wave speed ($V$ = 0.15 cm/ns), propagation distance ($L \approx 10$ cm), peak current ($I \approx 10$ A), and total coupled energy ($Q \approx 2.5$ mJ/pulse) are consistent with the experimental data**
- **Predicted plasma sheath thickness $\delta \approx 0.5$ mm, peak reduced electric field in the front and behind the wave $(E/N)_{peak} \approx 2000$ Td and $(E/N)_{res} \approx 200$-300 Td, respectively**

# Plasma ICCD images (quartz surface, positive polarity)



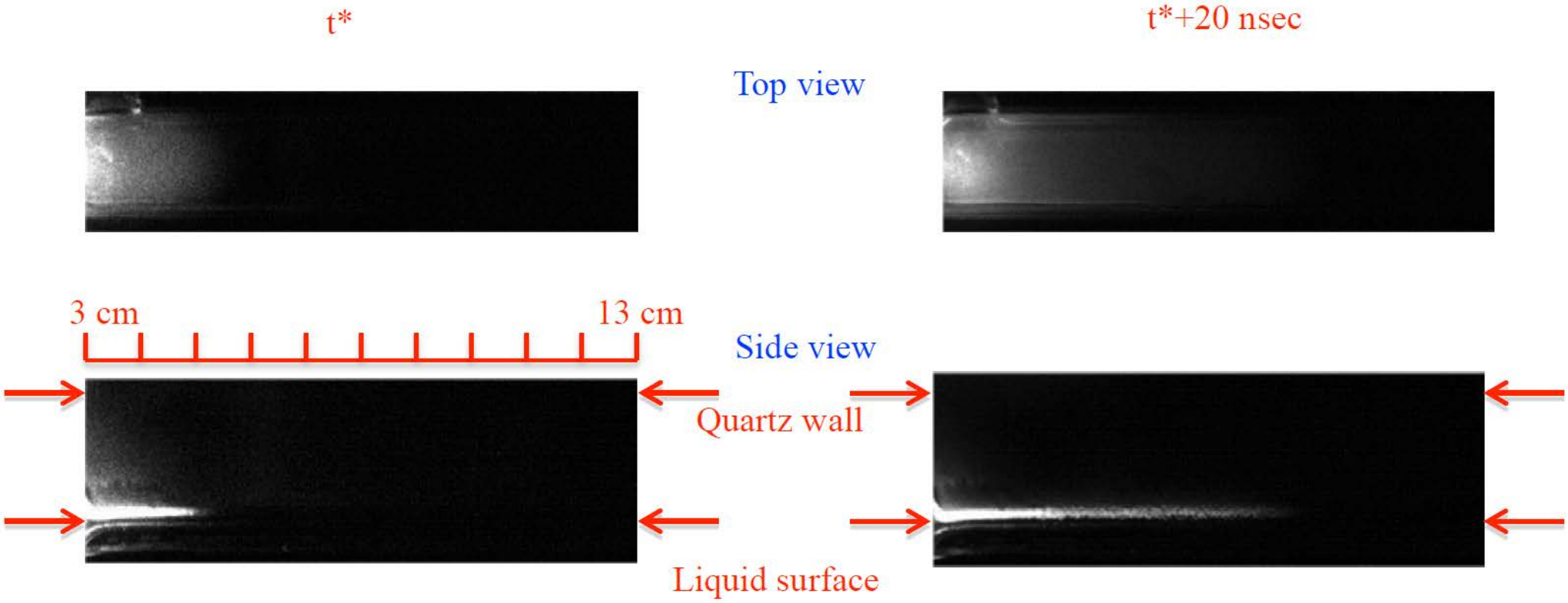

- $N_2$ buffer, P=20 Torr, flow rate 0.2 SLM, positive pulse polarity, wave over solid dielectric (quartz)
- Two different time delays shown, camera gate 10 nsec
- Side view and top view images taken simultaneously, using a mirror placed over the channel
- Diffuse plasma over the quartz surface (bottom wall of the channel)

# Plasma ICCD images (quartz surface, negative polarity)



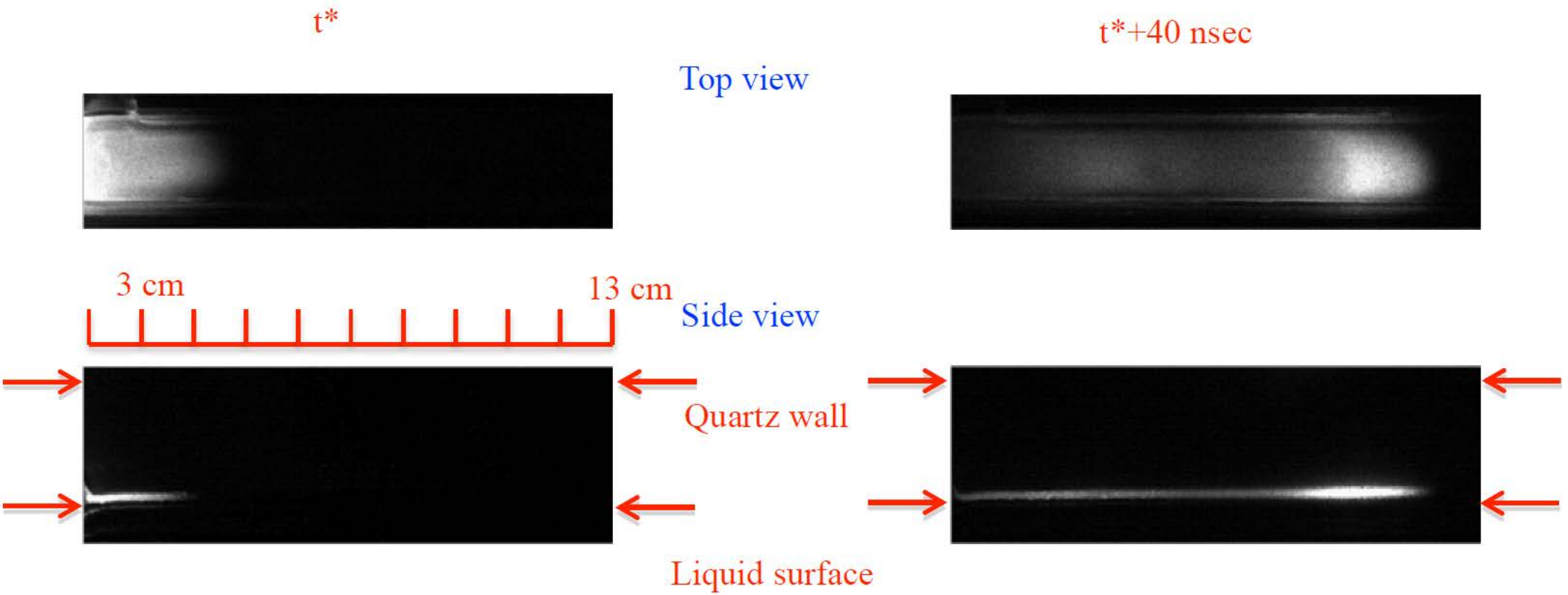

- $N_2$ buffer, P=20 torr, flow rate 0.2 SLM, positive pulse polarity, wave over solid dielectric (quartz)
- Two different time delays shown, camera gate 10 nsec
- Side view and top view images taken simultaneously, using a mirror placed over the channel
- Diffuse plasma over the quartz surface (bottom wall of the channel)

# Plasma ICCD images (distilled water, positive polarity)



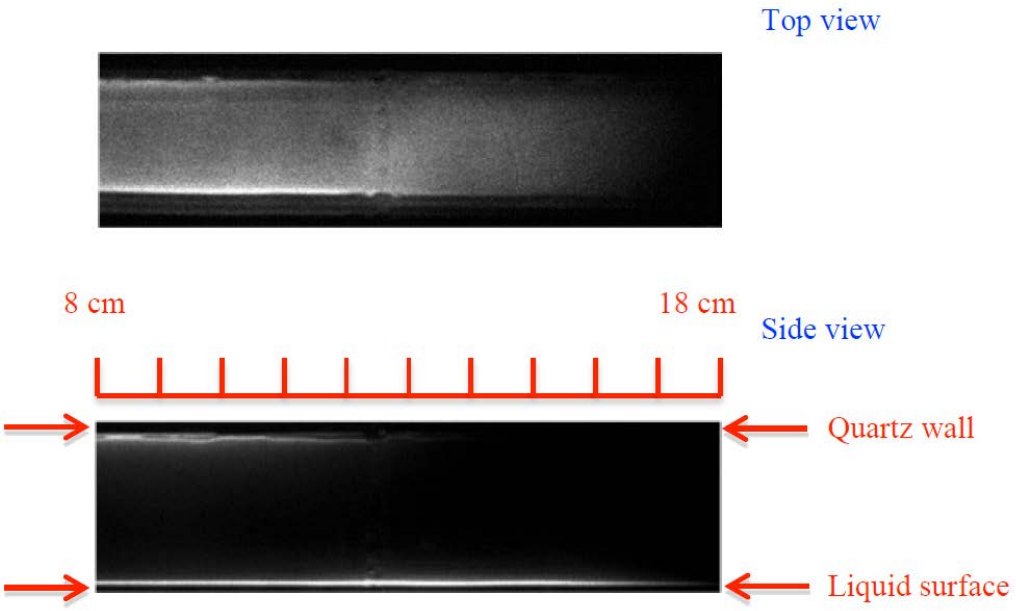

- $N_2$ buffer, P=20 torr, flow rate 0.2 SLM, positive pulse polarity, wave over distilled water
- Two different time delays shown, camera gate 10 nsec
- Side view and top view images taken simultaneously, using a mirror placed over the channel
- Diffuse plasma over the liquid surface (bottom wall of the channel)
- No liquid surface perturbation detected

# Plasma ICCD images (distilled water, negative polarity)

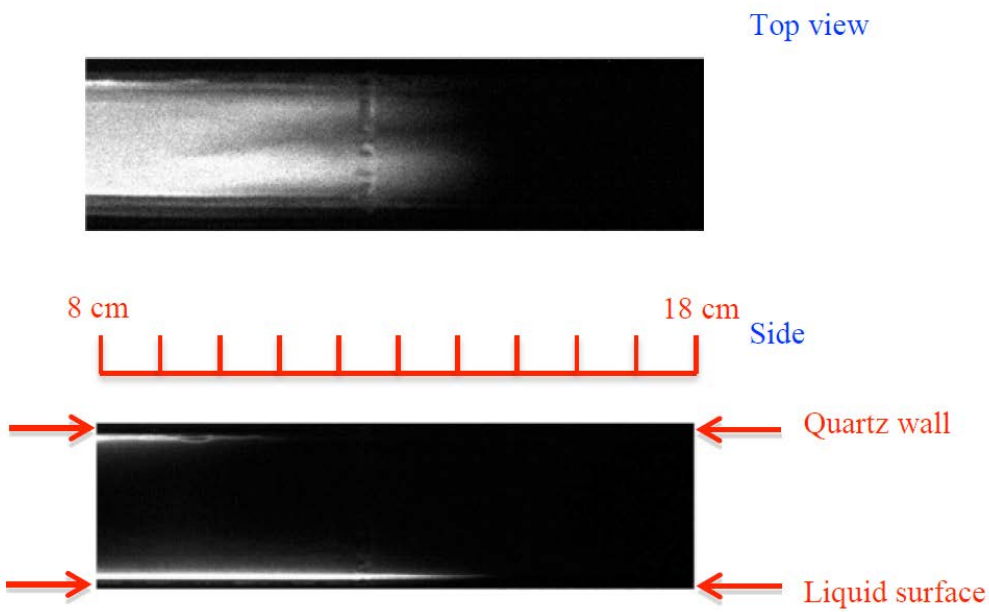



- $N_2$ buffer, flow rate 0.2 SLM, negative pulse polarity, wave over distilled water
- Two different time delays shown, camera gate 10 nsec
- Side view and top view images taken simultaneously, using a mirror placed over the channel
- Diffuse plasma over the liquid surface (bottom wall of the channel)
- No liquid surface perturbation detected

# Plasma ICCD images (butanol)



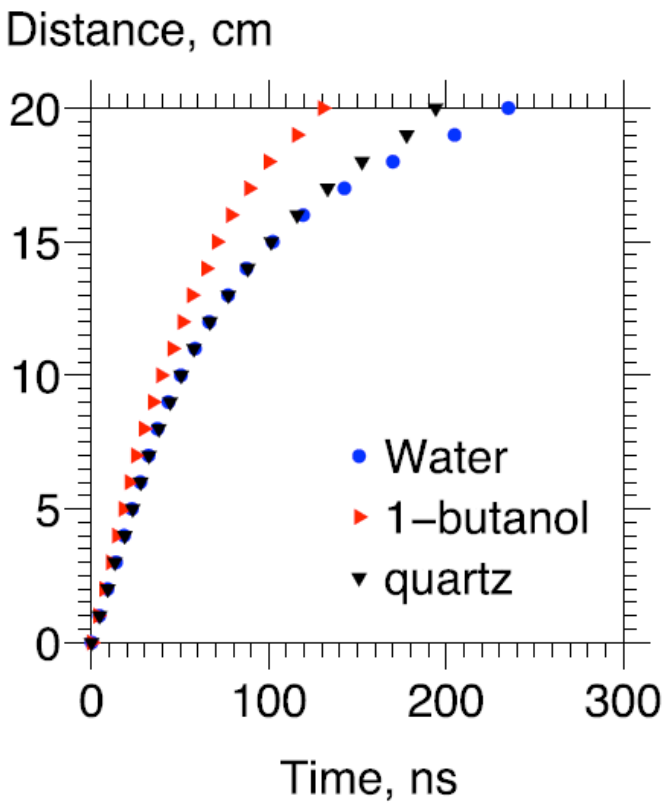

Positive polarity pulse

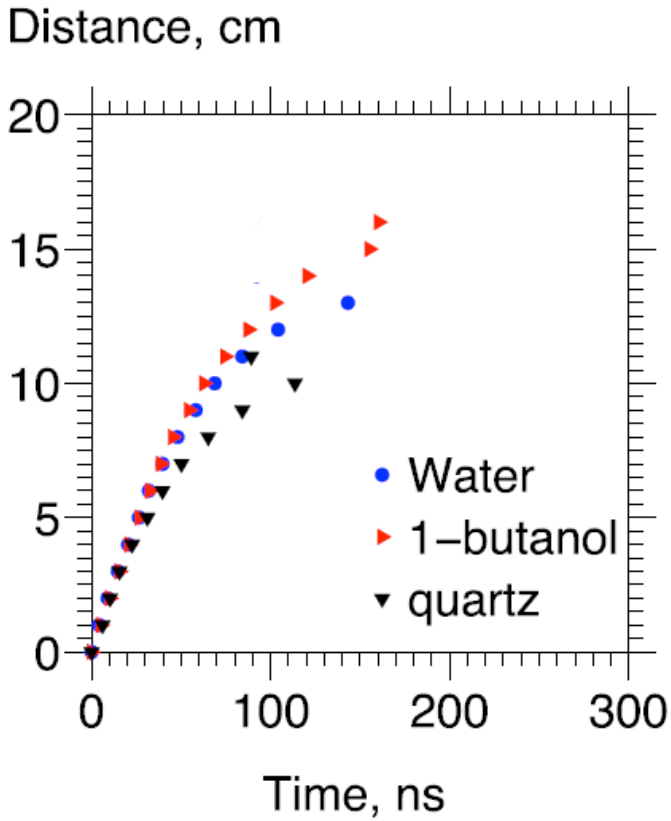



Negative polarity pulse

- $N_2$ buffer, P=20 torr, flow rate 0.1 SLM, wave over butanol
- Two different time delays shown, camera gate 10 nsec
- Side view and top view images taken simultaneously, using a mirror placed over the channel
- Diffuse plasma over the liquid surface (bottom wall of the channel) and quartz (top wall of the channel)
- No liquid surface perturbation detected

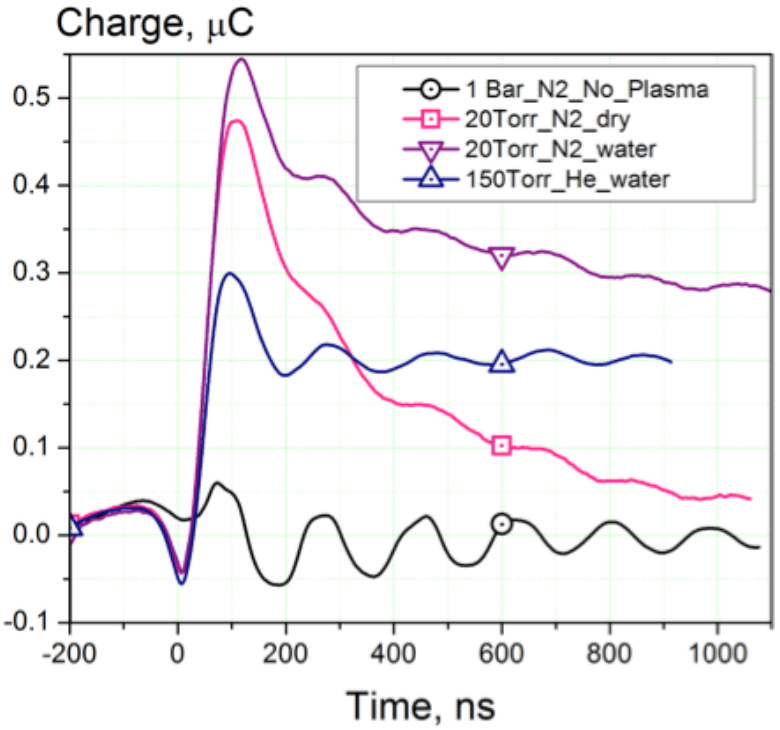
# Surface ionization speed measurement summary

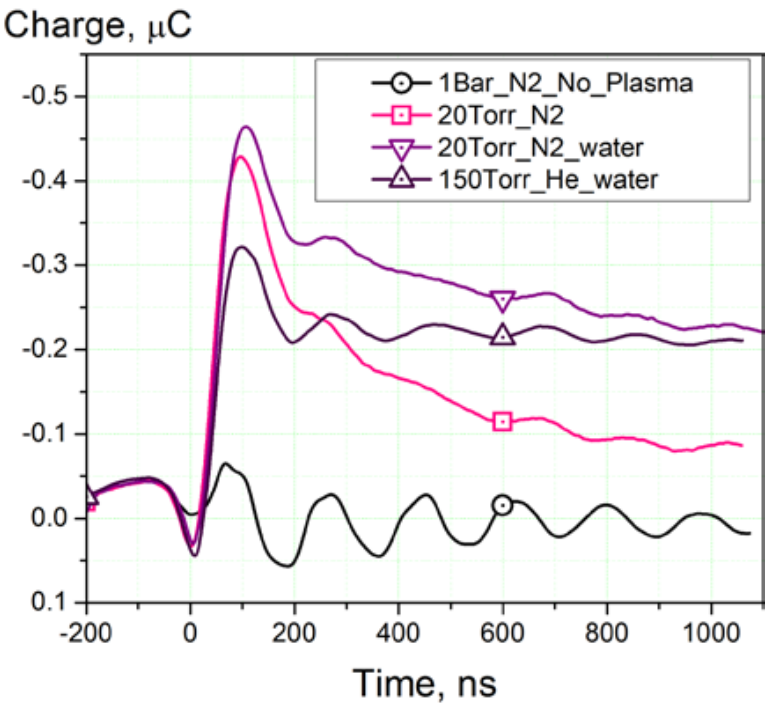



- **Positive polarity (left) wave speed, propagation distance are higher compared to negative polarity (right) wave speed, propagation distance**
- **Fairly little difference between wave speeds over quartz and liquid surfaces**
- **Surface plasmas always remain diffuse, although differences in emission intensity distributions are apparent**

# Net surface charge measurement summary



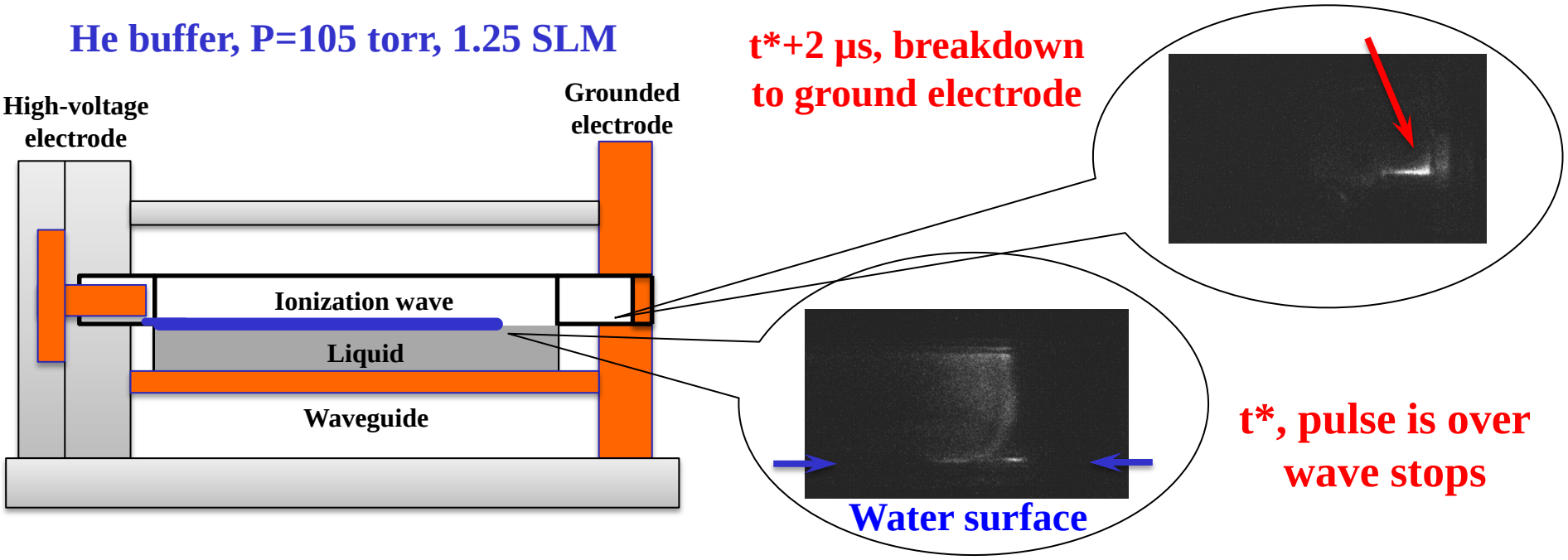

- Net surface charge obtained from conduction current waveforms, for entire discharge cell
- Positive polarity (left) waveforms are similar to negative polarity (right) waveforms
- Peak surface charge for distilled water is somewhat higher compared to quartz
- Surface charge decay time for distilled water (> 1 μs) is longer compared to quartz (~ 200 ns)
- More accurate measurements using a surface charge sensor are underway
- Does long-term surface charge accumulation occur? Surface charge removal through the bulk of liquid, due to finite conductivity ($\sigma \approx 10^{-4}$ S/m for water at the present conditions)

# Surface charge removal mechanisms after the pulse

- Characteristic time for surface charge removal from distilled water layer:

$$\tau_{RC} = RC \sim \frac{\varepsilon_Q \varepsilon_0}{\sigma} \frac{L^2}{d_Q d_L} \sim 1\ ms$$

- Delay time between pulses 5-10 ms, longer compared to $\tau_{RC}$: charge accumulation not an issue. Difference between waves produced by same polarity and alternating polarity pulse trains insignificant (may well change at high rep rate, due to surface charge neutralization)
- In addition, evidence of surface charge removal from liquid water surface after discharge pulse: breakdown to grounded electrode a few μsec after the pulse



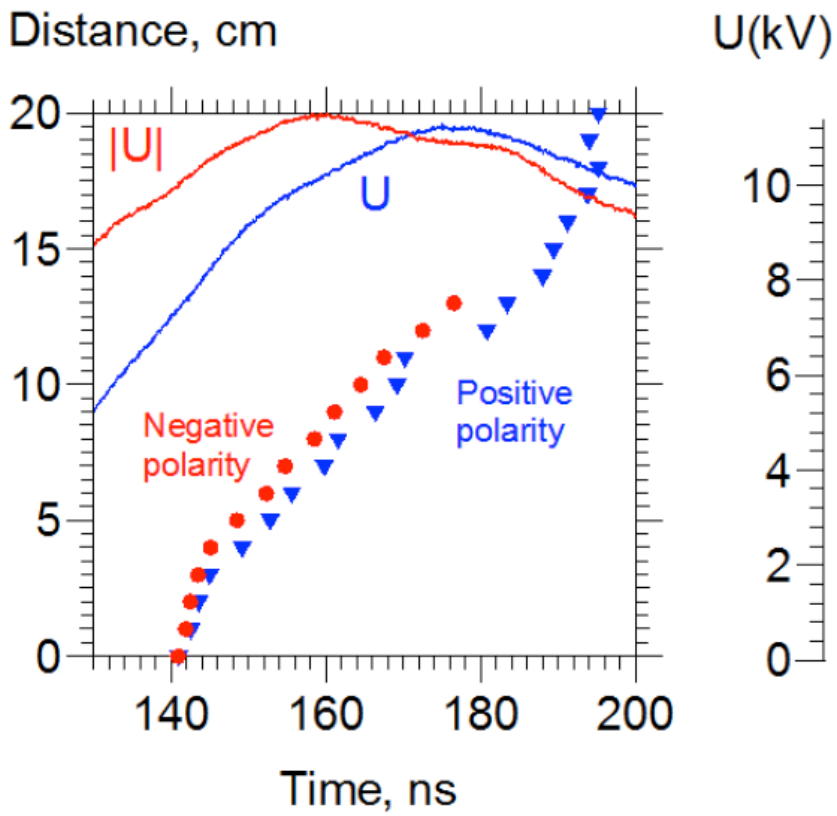
# Present experimental conditions: surface ionization wave plasma sustained in saturated vapor

- Laminar, fully developed flow
- Sherwood number for mass transfer (same as Nusselt number for heat transfer):

$$Sh_{\Delta} = \frac{hH}{D} = \frac{\left(\frac{d\rho}{dy}\right)_{surface}}{\rho_{surface} - \rho_{\infty}} \approx 3.0$$

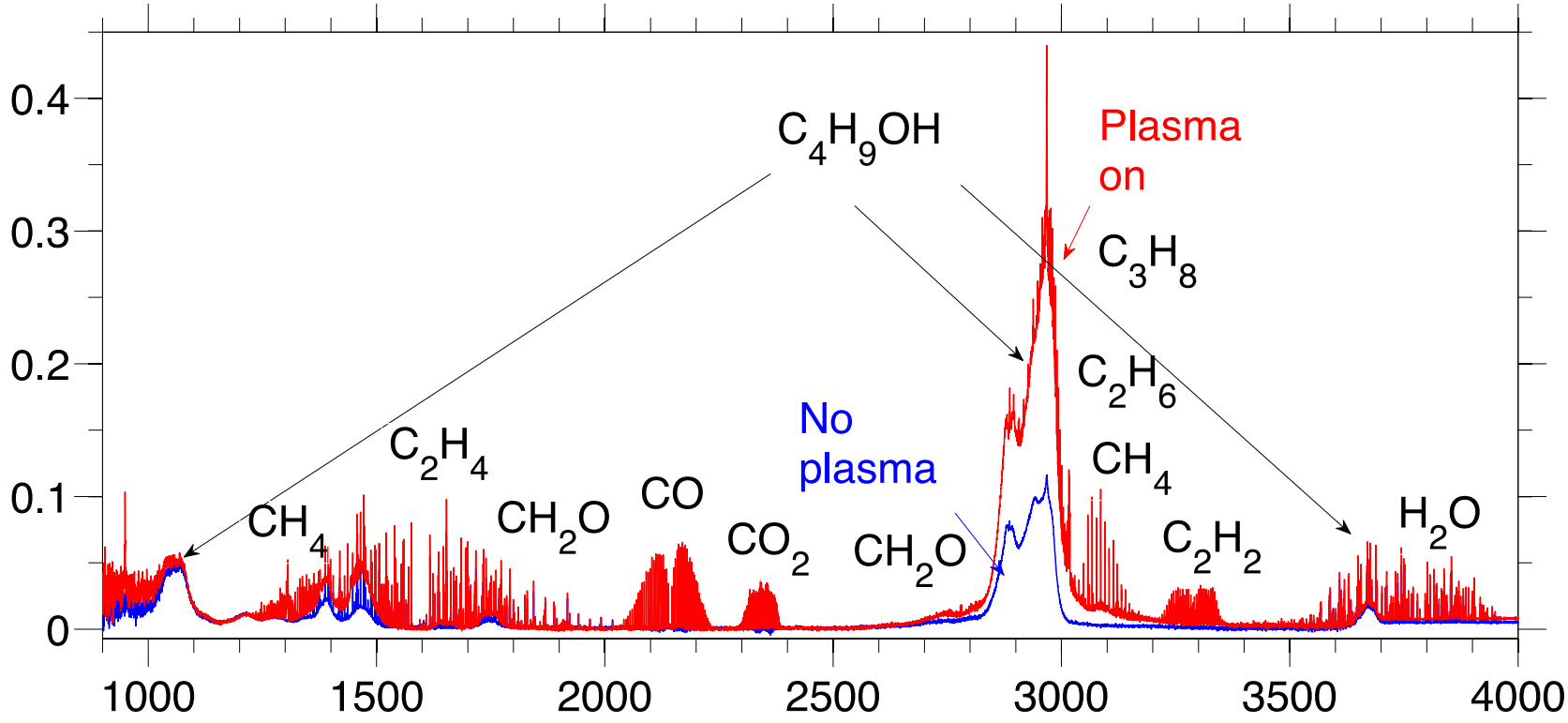
- Basically, at low buffer flow rates used, ~ 0.1 SLM, flow residence time, ~ 1 s , is much longer compared to water vapor diffusion time, ~ 0.1 s
- $(\rho_{sat} - \rho_{y=\delta})/(\rho_{sat} - \rho_{\infty}) \approx (\delta/H) \approx 10^{-2} << 1 \rightarrow \rho_{y=\delta} \approx \rho_{sat}$
- $P_{H2O} \approx P_{sat} \approx 17$ torr at $T=20^0$ C, $P_{H2O} \approx P_{total}$
- $P_{sat}$ is sensitive to the liquid temperature, $P_{sat}$ = 9 - 24 Torr at $T$ = 10 - 25 $^0$C
- Estimated liquid layer cooling at low flow rates used, ~ 0.1-0.2 SLM, is $\Delta T \approx$ 3-5 $^0$C
- Need to keep buffer flow rate low, to prevent excessive evaporative cooling, and even freezing, of liquid
- Strong electron affinity of water vapor is not a problem if reduced electric field is in the wave sufficiently high, $E/N$ > 130 Td, $\alpha(E/N) - \eta(E/N) > 0$

# Surface ionization wave in saturated butanol vapor ($P_{sat} \approx 5$ Torr, isolated cell, no flow)



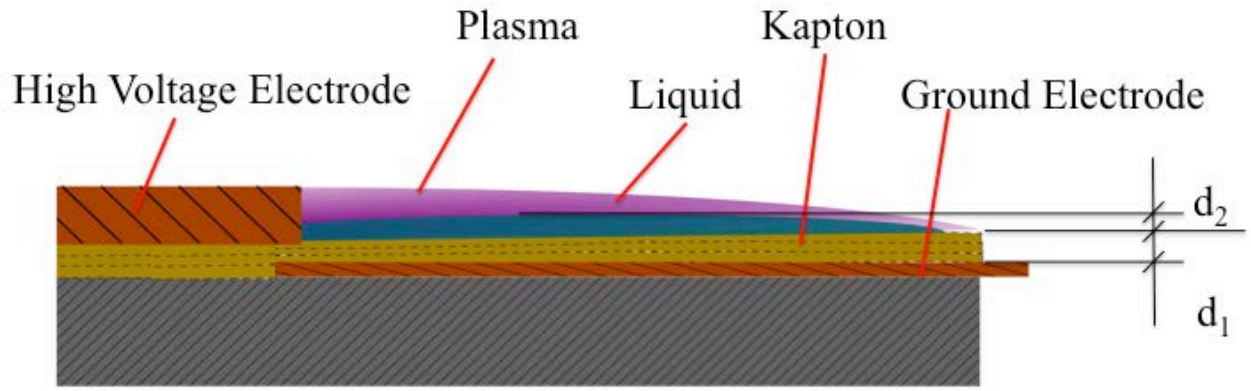

- Wave speed noticeably higher, $V \approx 0.27$ cm/ns over linear part of *x-t* trajectory (both for positive and negative pulse polarities), remains nearly constant throughout the channel
- Vapor / gas sample taken after 10 min operation at pulse rep rate of 500 Hz, analyzed by FTIR absorption spectroscopy

# FTIR absorption spectrum of stable products (wave in saturated butanol vapor, isolated cell, no flow)




- Butanol partial pressure remains the same as long as temperature in the discharge is the same (controlled by saturated vapor pressure, $P_{sat}(T)$): butanol bands should remain the same
- However, considerable increase of absorbance at location of 2850-3000 $cm^{-1}$ butanol band: significant conversion to propane
- Large variety of other products, partial pressures will be determined using synthetic spectra

# Unexpected spinoff: Nanosecond Pulse Surface DBD plasma actuators



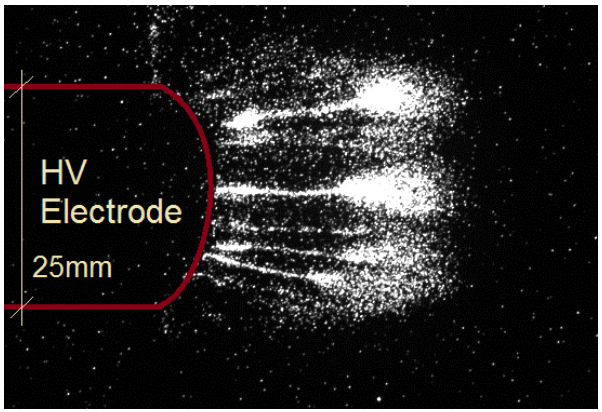

- **Surface charge accumulation is widely believed to be one of the factors limiting performance of NS-SDBD plasma actuators (such as coupled discharge pulse energy)**

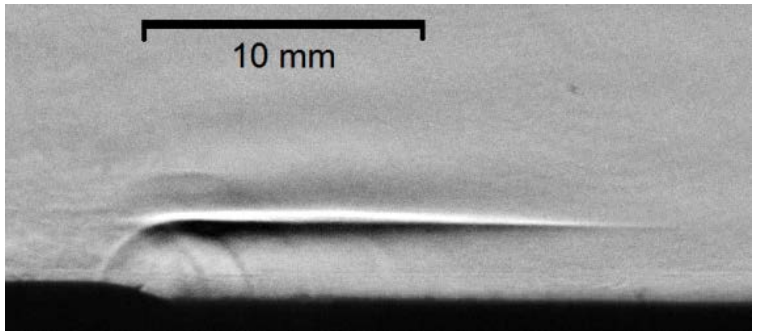
- **Semiconducting or partially conducting surface (such as a thin layer of liquid) can be used to "bleed off" excess surface charge between discharge pulses, without affecting actuator performance during the pulses**

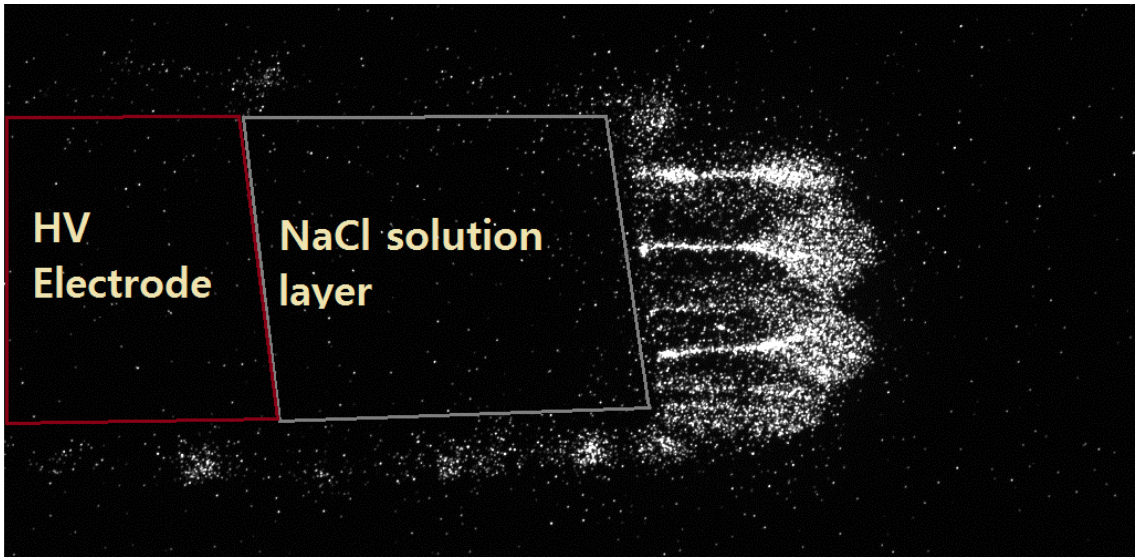
- **This is done if time for surface charge removal due to conduction through liquid, $\tau_{RC}$, is longer than pulse duration, $\tau_{pulse}$, but much than interval between pulses, $\tau_{delay}$: $\tau_{pulse} << \tau_{RC} << \tau_{delay}$ (i.e. the liquid is a dielectric during the pulse and a conductor between the pulses)**

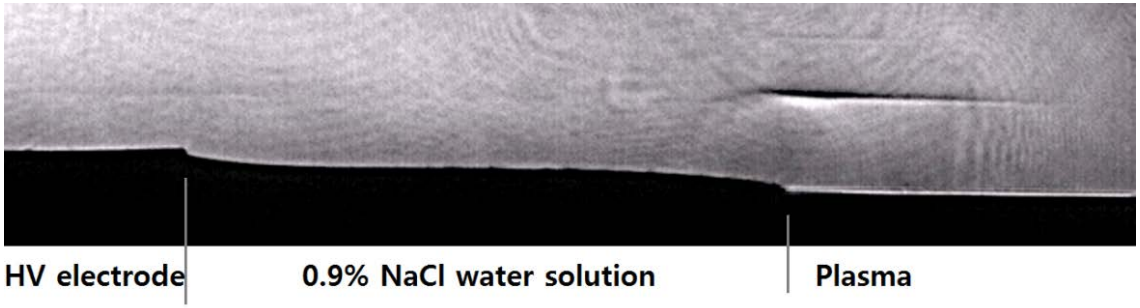
# Nanosecond pulse surface discharges in room air over Kapton dielectric and saline solution

- In the opposite limit (high-conductivity liquid, saline solution), $\tau_{pulse} >> \tau_{RC}$ , liquid layer acts simply as a high voltage electrode extension during the pulse



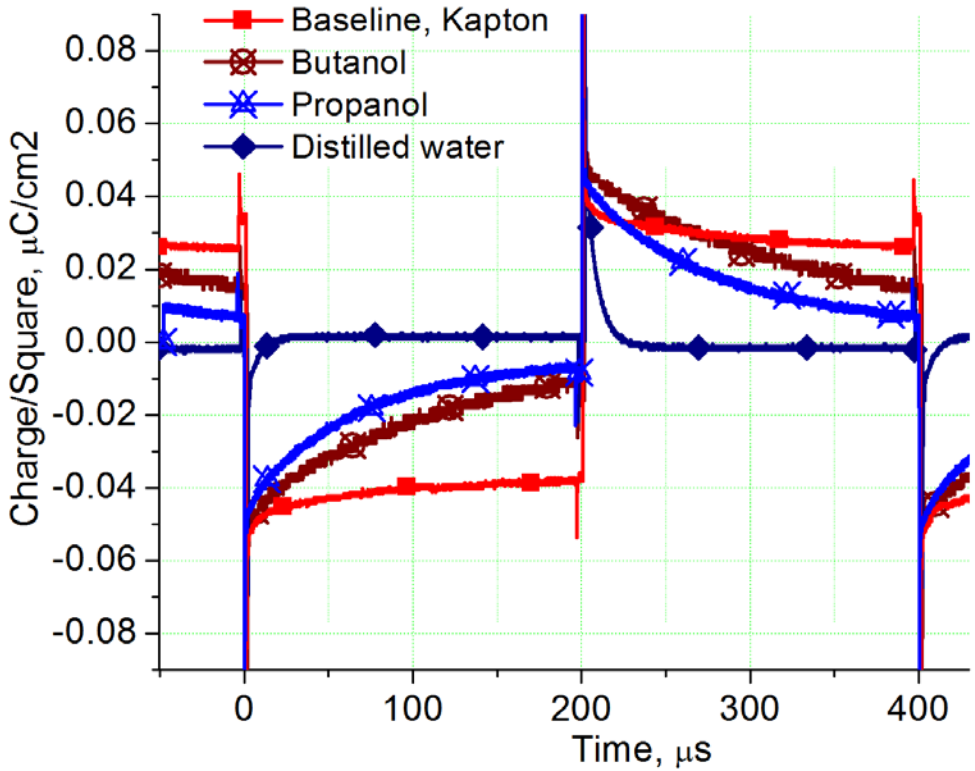

**Surface discharge over Kapton:**

**Plasma emission, compression wave start near electrode**

**Surface discharge over saline solution:**

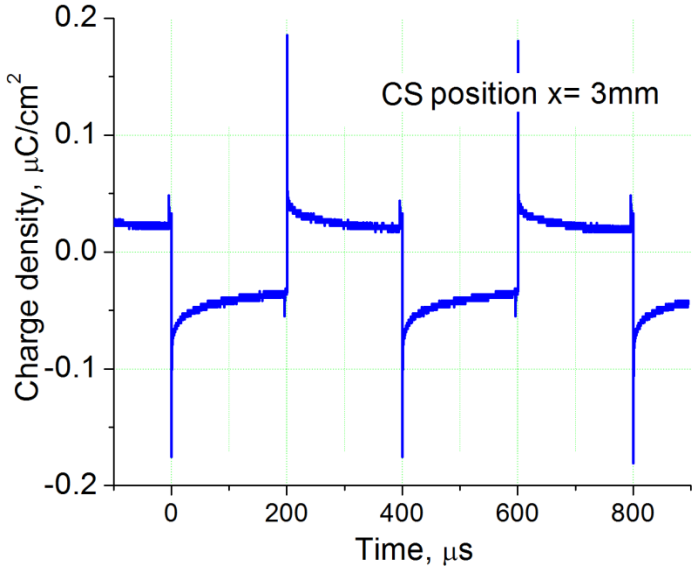
**Plasma emission, compression wave start near edge of liquid pool**

# NS-DBD surface charge "bleeding" between the pulses: Kapton dielectric vs. different liquids, room air

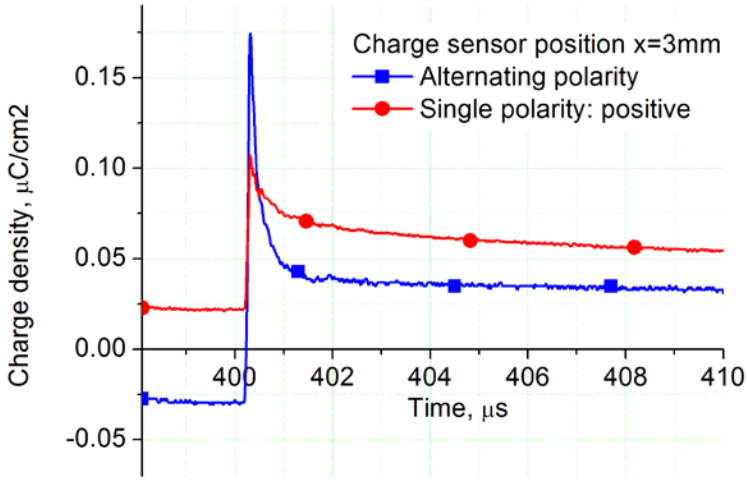


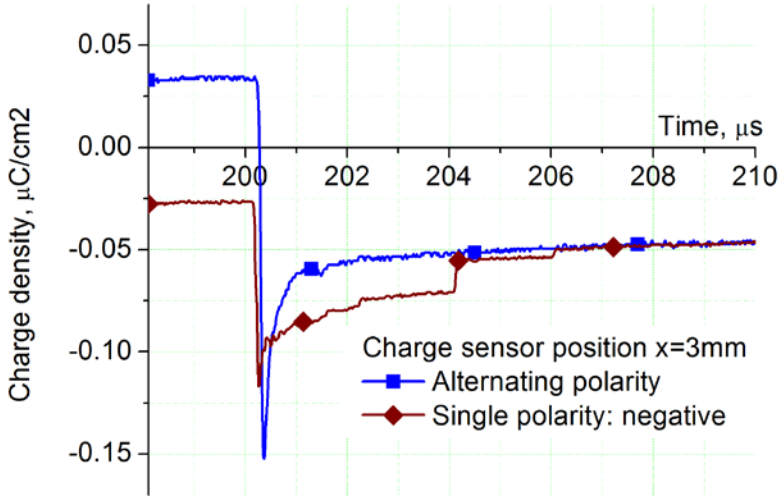

- Surface charge decay time, $\tau_{RC}$ : Kapton ≈ 2 ms, propanol ≈ 100 μs, distilled water ≈ 5 μs
- Pulse duration, $\tau_{pulse}$ ~ 100 ns; interval between pulses, $\tau_{delay}$ ~ 200 μs
- Distilled water acts a dielectric during the pulse, removes surface charge between pulses
- However, approximately half of discharge pulse energy is lost (to Joule heating of liquid)
- Is it really worth doing? Can there be another, loss-free, solution to the problem?

# Surface charge density in NS-DBD plasma actuators: alternating polarity vs. same polarity pulse trains




- Room air, alternating polarity pulse train (5 kHz)
- Residual surface charge from the previous pulse is neutralized by the next pulse
- Energy released is coupled to the plasma

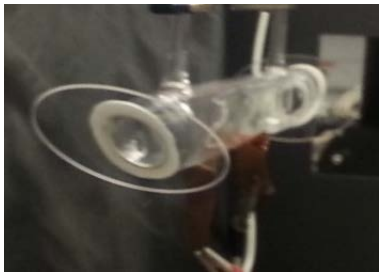


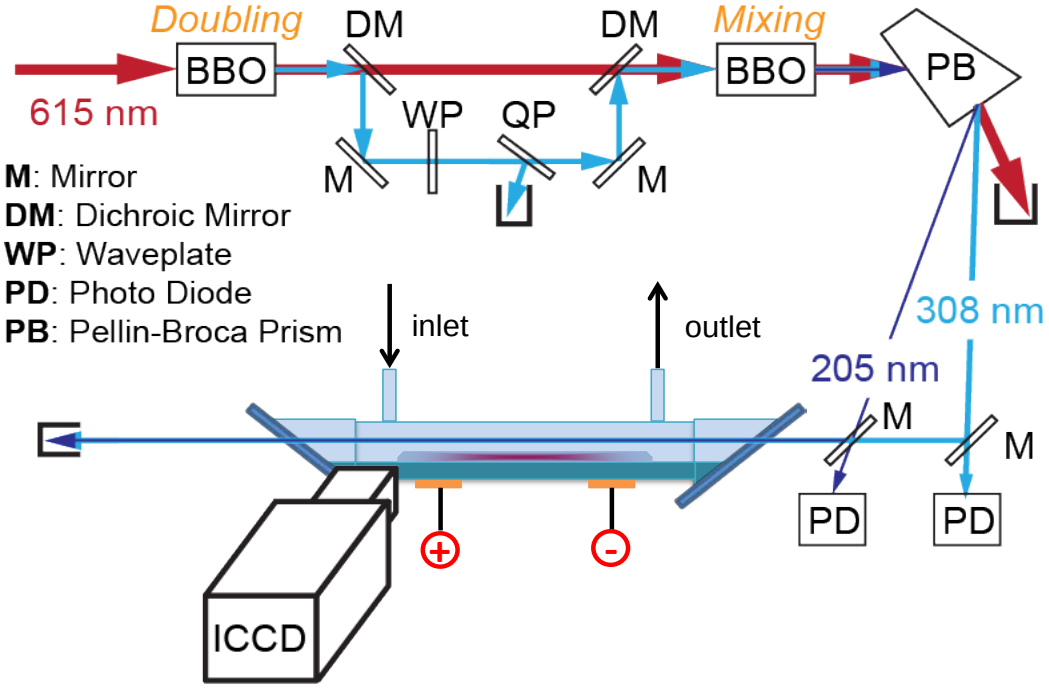




- Same polarity vs. alternating polarity pulses trains (zoomed in)
- Charge transferred during same polarity pulses a factor of ~ 2 lower, coupled energy a factor of ~ 4-5 lower (up to an order of magnitude in filamentary surface discharges)
- Use of alternating polarity pulse is far more efficient compared to surface charge "bleeding"

# On-going work: *in situ* radical species measurements at liquid-vapor interface

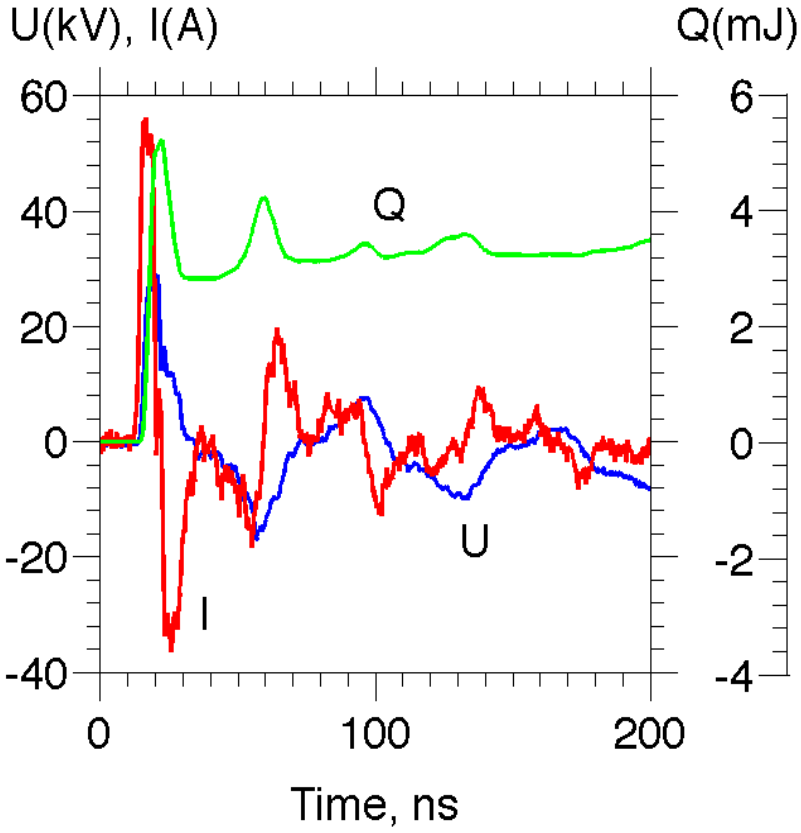
- Vapor / buffer flow over an evaporating liquid surface, T=300 K
- Water, aqueous solutions, liquid hydrocarbons / oxygenates
- Electrodes powered by ns discharge pulse, surface ionization wave plasmas
- Simple "canonical" geometry, ample optical access
- Diagnostics: *in situ*, time-resolved, absolute [OH], [NO] (LIF/PLIF); [H], [O], [N] (TALIF); *ex situ*, stable products (FTIR)





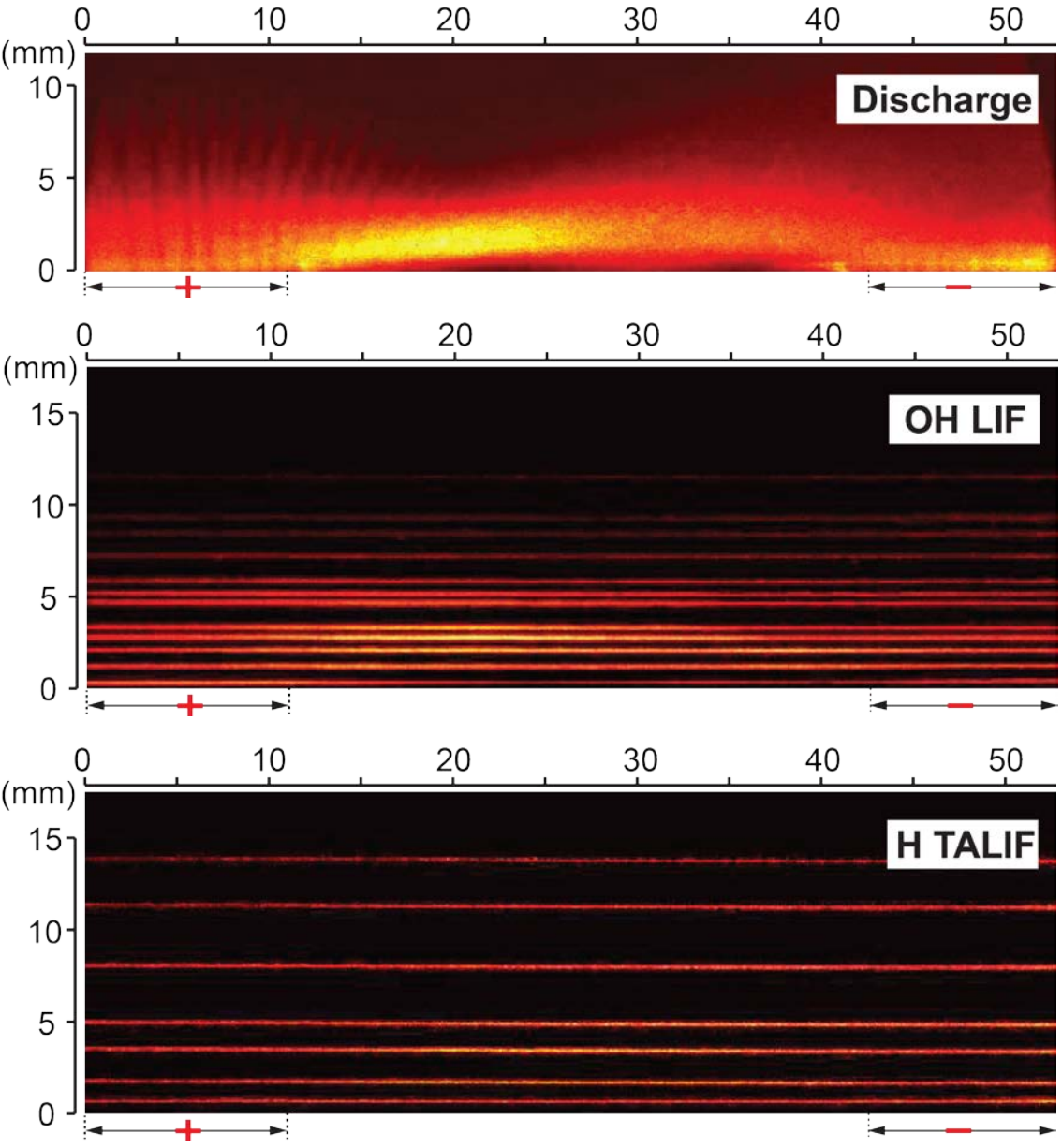

**Photos of liquid-vapor discharge cell, schematic of LIF / TALIF diagnostics**

# Discharge pulse waveforms




- Saturated $H_2O$ vapor / Ar buffer flow over liquid water surface (0.1 SLM), P=30 torr
- Electrodes powered by 20-pulse bursts (30 kV, 10 ns), pulse rep rate 1 kHz
- Voltage pulse sustained between positive and negative polarity electrodes (no ground)
- Voltage, current and coupled energy traces (pulse #19 in a burst of 20 pulses, rep rate 1 kHz)
- Energy coupled by main pulse and several reflected pulses

# Radicals in liquid-vapor interface plasma: ICCD, OH LIF, H TALIF line images

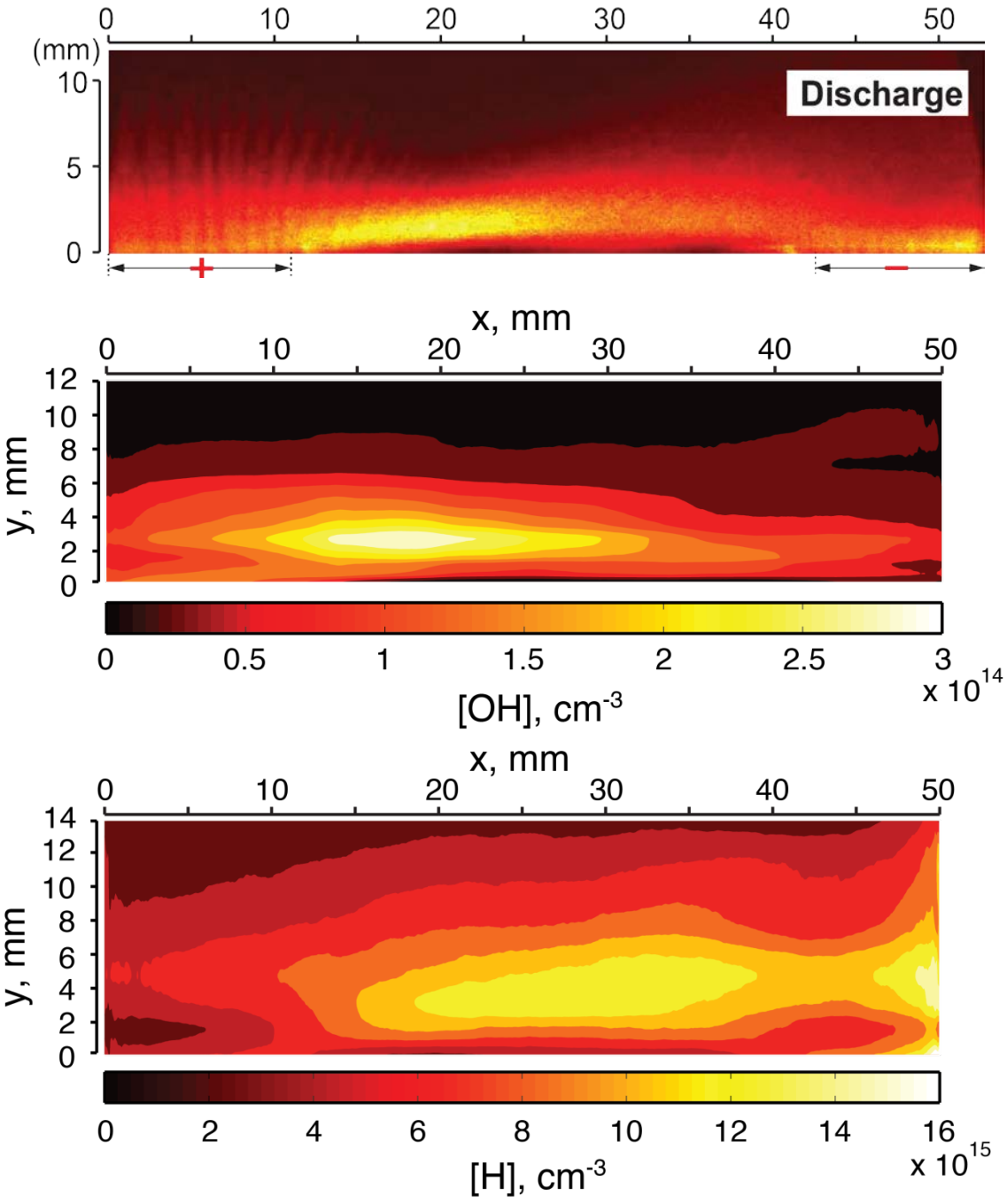



Positive electrode

Negative electrode

- Plasma is somewhat “lifted” from the liquid surface
- ICCD, OH LIF, and H TALIF line images, liquid water surface at y = 0
- Line images shown vs. height over liquid surface, y ≈ 300 μm to y = 15 mm
- Sets of line images are used to obtain 2-D contour plots of LIF and TALIF signal distributions

# Radicals in liquid-vapor interface plasma: 2-D distributions of absolute [OH], [H]




- Absolute calibration: Rayleigh scattering (OH LIF), Kr reference (H TALIF)
- Low laser power to avoid saturation, photo-ionization, and photolytic effect
- Total number density: $10^{18}$ $cm^{-3}$
- Peak [OH] = $3 \cdot 10^{14}$ $cm^{-3}$
- Peak [H] = $1.6 \cdot 10^{16}$ $cm^{-3}$ , [H] >> [OH]
- H decay reaction, $H + H + M \rightarrow H_2 + M$ , is much slower compared to OH decay reaction, $OH + OH \rightarrow H_2O + O$
- OH distribution follows plasma emission intensity
- H atoms diffuse / convect further away from liquid surface, generation region
- On-going measurements: NO PLIF
- Planned measurements: O, N TALIF

# Summary

- Surface ionization wave discharges generated by high-voltage nanosecond pulses, over quartz surface and dielectric liquid surfaces (water and butanol) are studied
- Ionization waves propagate predominantly over quartz or liquid surface adjacent to grounded waveguide
- Surface plasma “sheet” is diffuse and highly reproducible, for positive and negative polarities
- Parameters of ionization wave discharge over water and quartz surfaces are similar. Positive polarity waves propagate at higher speed, over longer distance, compared to negative polarity waves.
- Wave speed, propagation distance decrease with pressure
- No perturbation of the liquid surface was detected
- Rapid removal of surface charge between pulses: conduction through liquid, surface breakdown to grounded electrode
- At low buffer flow rates, surface wave plasmas sustained in saturated vapor
- Plasma chemical reaction products accumulated in surface wave discharge over liquid butanol / saturated butanol vapor detected from FTIR absorption spectra. Products include CO, alkanes, alkynes, aldehydes, and lighter alcohols

# Summary / Ongoing Work

- NS-DBD plasma actuators: use of alternating polarity pulse trains is far more efficient compared to surface charge “bleeding”
- Alternating polarity pulses: residual surface charge from previous pulse is neutralized by next pulse, energy released is coupled to the plasma
- Surface charge “bleeding”: significant loss of coupled pulse energy to waste Joule heating
- Alternating polarity pulse train couples considerably higher energy per pulse, compared to same polarity pulse train
- Measurements of absolute, time-resolved, 2-D distributions of radicals generated in ionization wave plasmas at liquid vapor interface (water, aqueous solutions, alcohols, hydrocarbons)
- Insight into fundamental kinetics of plasma chemical reactions at liquid-vapor interface
- Possible applications: biomedical, liquid hydrocarbon fuel reforming, plasma flow control

# Acknowledgments

**NSF** ***"Kinetics of Non-Equilibrium Fast Ionization Wave Plasmas in Gas Phase and Gas-Liquid Interface"***

**US DOE Plasma Science Center** ***"Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems"***

**AFOSR MURI** ***"Fundamental Mechanisms, Predictive Modeling, and Novel Aerospace Applications of Plasma Assisted Combustion"***