Studies of nanosecond pulse surface ionization wave discharges over solid and liquid dielectric surfaces

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Abstract
Surface ionization wave discharges generated by high-voltage nanosecond pulses, propagating over a planar quartz surface and over liquid surfaces (distilled water and 1-butanol) have been studied in a rectangular cross section test cell. The discharge was initiated using a custom-made, alternating polarity, high-voltage nanosecond pulse plasma generator, operated at a pulse repetition rate of 100–500 Hz, with a pulse peak voltage and current of 10–15 kV and 7–20 A, respectively, a pulse FWHM of ~100 ns, and a coupled pulse energy of 2–9 mJ/pulse. Wave speed was measured using a capacitive probe. ICCD camera images demonstrated that the ionization wave propagated predominantly over the quartz wall or over the liquid surface adjacent to the grounded waveguide placed along the bottom wall of the test cell. Under all experimental conditions tested, the surface plasma 'sheet' was diffuse and fairly uniform, both for positive and negative polarities. The parameters of ionization wave discharge propagating over distilled water and 1-butanol surfaces were close to those of the discharge over a quartz wall. No perturbation of the liquid surface by the discharge was detected. In most cases, the positive polarity surface ionization wave propagated at a higher speed and over a longer distance compared to the negative polarity wave. For all three sets of experiments (surface ionization wave discharge over quartz, water and 1-butanol), wave speed and travel distance decreased with pressure. Diffuse, highly reproducible surface ionization wave discharge was also observed over the liquid butanol–saturated butanol vapor interface, as well as over the distilled water–saturated water vapor interface, without buffer gas flow. No significant difference was detected between surface ionization discharges sustained using single-polarity (positive or negative), or alternating polarity high-voltage pulses. Plasma emission images yielded preliminary evidence of charge removal from the liquid surface between the pulses on a microsecond time scale. Products of the plasma chemical reaction that accumulated in the ionization wave discharge over the liquid butanol–saturated butanol vapor interface were detected ex situ, using FTIR absorption spectroscopy. Reaction products identified include CO, alkanes (CH₄, C₂H₆, C₃H₈), alkynes (C₂H₂), aldehydes (CH₂O) and lighter alcohols (CH₃OH).

Keywords: electric discharges, surface ionization waves, liquid–vapor interface, plasma chemistry

(Some figures may appear in colour only in the online journal)

1. Introduction

The kinetics of nonequilibrium electric discharges in liquids and at liquid–vapor interfaces is of great interest from the fundamental viewpoint [1] and is of critical importance for the development of applications such as reactive nitrogen–oxygen species generation [2], plasma activation of water for sterilization and wound treatment [3, 4], removal of volatile
organic compounds from water and aqueous solutions [5, 6] and plasma chemical reforming of liquid hydrocarbons and oxygenates for portable fuel cells [7–10], proposed as an alternative to thermo-catalytic fuel reforming. In spite of the extensive experimental (e.g. see [1] and references therein) and modeling (e.g. see [6, 11, 12]) studies of nonequilibrium plasmas generated in the presence of liquids, the kinetics of plasma chemical reactions under these conditions remains poorly understood. One of the main difficulties encountered in quantitative studies of liquid–vapor phase plasma chemistry is sustaining the plasma at controlled, well-reproducible, ample optical access conditions, which would lend themselves to in situ, time- and spatially resolved optical diagnostics. Typically, in the experiments the liquid–vapor interface plasma is generated away from the liquid surface [4], or sustained as a stochastic manifold of streamers propagating in the vapor phase [5], in the bulk of the liquid [6, 9] (usually via microscopic bubbles although formation of plasma in the liquid phase has been suggested [13]), in macroscopic bubbles [14], or over the liquid surface [15, 16]. Quantifying the plasma parameters, as well as accurate time- and spatially resolved species concentration measurements under these conditions is extremely difficult. Lack of in situ measurements of the plasma parameters under well-characterized conditions also hinders the development and validation of kinetic models, and assessing their predictive capability.

In this work, a novel way of sustaining diffuse, highly reproducible plasmas at liquid–vapor interfaces is demonstrated, using surface ionization waves generated by high-voltage, nanosecond pulse duration discharges. The basic concept of this approach is qualitatively similar to volumetric and surface fast ionization wave (FIW) nanosecond pulse discharges, which are known to generate diffuse plasmas over large volumes or large surface areas, in a wide range of pressures [17, 18]. Typically, the wave amplitude attenuation rate is fairly low due to the high electrical conductivity of the plasma column (or near-surface plasma sheet) behind the wave, which essentially acts as an extension of the high-voltage electrode. The fundamental difference between FIW plasmas and other types of nonequilibrium plasmas is the high peak electric field in the wave front (up to $E/N \sim 1000\, \text{Td} = 10^{-14}\, \text{V cm}^{-2}$). High overvoltage in the presence of weak residual ionization results in the development of a nearly planar ionization wave front, instead of isolated streamer breakdown [17, 18]. The high electron energy achieved in the wave front significantly accelerates electron impact processes with a high energy threshold, such as ionization and molecular dissociation, thus generating reactive radical species in molecular plasmas. Also, at the high peak electron energies involved, the rate of electron impact ionization greatly exceeds the rate of dissociative attachment, such that diffuse plasmas can be sustained even in strongly electronegative gases mixtures, such as water vapor. Finally, the high wave speed (of the order of $\sim 0.1–1\, \text{cm s}^{-1}$) greatly enhances plasma stability, since ionization instabilities do not have time to develop during the wave front residence time.

The short time scales involved in surface ionization wave discharges launched over the surface of a dielectric, or weakly conductive, liquid (typically $\sim 10–100\, \text{ms}$) preclude bulk motion of the liquid that may be caused by charge accumulation on the liquid surface. In addition, net surface charge accumulation may be controlled and significantly reduced by alternating the high-voltage pulse polarity and by using a weakly conductive liquid. The peak electric field in the surface ionization wave may be further enhanced if the discharge is generated over a liquid with a high dielectric constant. Under these conditions, high energy electrons generated in the thin near-surface plasma layer initiate electron impact dissociation and ionization of evaporating reactants, with a potentially high yield of radical species, such as O, H and OH in surface plasmas sustained over liquid water and aqueous solutions, and CH in surface plasmas over liquid hydrocarbons and oxygenates. The yield of these reactions may be enhanced considerably by operating the discharge with a high velocity of buffer gas flowing above the liquid surface, under conditions in which the net rate of evaporation is high. The generation of the initial radical pool may result in a rich plasma chemistry and the formation of a variety of stable product species, depending on the initial composition of the liquid and the buffer gas flow. Note that chemical reactions in repetitively pulsed plasma at a liquid–vapor interface would occur at nearly constant temperature conditions, since Joule heating would be limited by both the high specific heat of the liquid and the high latent heat of vaporization ($\sim 0.4\, \text{eV/molecule for water and alcohols}$). This all suggests that a surface ionization wave discharge plasma sustained at a liquid–vapor interface can be used as an experimental platform for studies of near-surface plasmachemical reaction kinetics, under conditions where the interface acts as a high-yield ‘planar surface source’ of radical species. Currently, the kinetics of these reactions, as well as the time evolution of the electric field and electron density distributions along the interface, remain largely unknown.

The main objective of this work is to determine the range of conditions where nanosecond pulse, diffuse surface ionization wave discharges propagate along liquid–vapor interfaces and to demonstrate the significant potential of this approach for studies of near-surface plasma chemical reactions, in particular electron impact processes generating reactive radical species from evaporating liquid reactant, and their subsequent conversion into stable product species.

2. Experimental details

The experimental apparatus used for the studies of surface ionization wave discharges is shown in figure 1. The discharge is sustained in a rectangular cross section quartz channel with width $W = 25\, \text{mm}$, height $H = 35\, \text{mm}$, length $L = 220\, \text{mm}$ and walls $d_{0} = 1.75\, \text{mm}$ thick, with a trough in the bottom which can be filled with liquid (see figure 1(a)). Two 8 mm diameter quartz tubes are fused to the side wall of the channel near the bottom to provide the means of filling it with liquid and draining it, as shown in figure 1(b). In these experiments, the liquids used are distilled water and 1-butanol. Butanol was chosen over lighter alcohols (methanol and ethanol) due to its relatively low saturated vapor pressure, $P_{\text{sat}} = 4.8\, \text{Torr}$ at $T = 20\, ^{\circ}\, \text{C}$. In all the experiments, the liquid layer thickness
is approximately $d_L = 5\text{ mm}$. At both ends, the rectangular section of the channel is fused with cylindrical quartz tubes with a 25 mm outer diameter, to enable a vacuum seal with the rest of the apparatus. The high-voltage electrode on the left is a hollow cylinder made of copper, with a 10 mm inner diameter, 12 mm outer diameter and length of 32 mm, connected to a circular copper plate 45 mm in diameter. The electrode is mounted between two Teflon flanges providing a vacuum seal and electrical isolation, as shown in figure 1(a). The vertical distance from the high-voltage electrode to the liquid surface and to the top wall of the quartz channel is approximately 10 mm. The grounded electrode on the right is a 100 mm $\times$ 100 mm $\times$ 16 mm copper flange with a circular port 25 mm in diameter. The distance between the high-voltage electrode and grounded electrode is 280 mm. The Teflon flanges holding the high-voltage electrode and the grounded electrode flange are mounted on a base plate made of glass fiber reinforced plastic.

An adhesive copper foil electrode is attached to the bottom wall of the quartz channel and connected to the grounded electrode (see figure 1(a)), to operate as a waveguide for the surface ionization wave discharge. The role of the grounded waveguide is to maintain a strong transverse electric field over the dielectric (solid or liquid) surface ahead of the surface ionization wave, and thus sustain ionization in the wave front [17]. Thus, the proximity of the waveguide to the dielectric surface over which the wave is propagating is critically important. Basically, the parameter controlling the wave speed is the ‘effective’ value of the dielectric layer thickness, $d_{\text{eff}} = d_Q/\varepsilon_Q + d_L/\varepsilon_L$ [17]. For waves propagating over quartz and water, the effective thickness in both cases is essentially the same, since $d_Q/\varepsilon_Q \approx 1.75\text{ mm}/3.8 \approx 0.46\text{ mm}$, while $d_L/\varepsilon_L \approx 5\text{ mm}/80 \approx 0.06\text{ mm}$. In butanol, the effect of adding the liquid layer is somewhat more pronounced due to its lower dielectric constant, $\varepsilon_L \approx 18$, such that $d_L/\varepsilon_L \approx 0.28\text{ mm}$, i.e. $d_{\text{eff}}$ increases by $\sim 50\%$. The waveguide covers the entire width of the rectangular channel, which is sufficient to sustain the plasma over the entire width of the liquid surface. Moving the waveguide further away from the surface (by 15 mm) considerably reduces the surface ionization wave uniformity, such that it propagates predominantly along the two bottom corners of the rectangular channel, where the electric field is higher.

The electrodes are powered by a custom-made high-voltage nanosecond pulse generator which produces alternating (positive/negative) polarity pulses with a peak voltage of $\sim 10$–$20\text{ kV}$ and a FWHM pulse duration of $\sim 50$–$100\text{ ns}$, at a pulse repetition rate of up to $50\text{ kHz}$ [19, 20]. In these
experiments, the pulse generator is operated at pulse repetition rates ranging from 100–500 Hz, using an external trigger produced by an Instek AFG-2125 function generator. The pulse peak voltage is controlled by varying the pulser input dc voltage provided by a Glassman EH series dc power supply (1000 V, 100 mA). Some of the experiments are conducted with only positive or only negative polarity pulses applied to the high-voltage electrode, with UF1007-T ultrafast rectifier diodes connected in series between the high-voltage terminal of the pulser and the high-voltage electrode in the test cell (35 diodes rated for 1 kV peak voltage each). Output pulse voltage is measured by a Tektronix P6012A high-voltage probe, connected between the high-voltage electrode and the grounded electrode. Pulse current is measured using a Pearson 2877 current probe, placed on the high-voltage cable connecting the pulser and the high-voltage electrode, as shown in figure 1.(b).

A buffer gas (nitrogen or helium), supplied from gas cylinders, flows through the test cell from the grounded electrode toward the high-voltage electrode. The flow rate through the test cell is measured either by a Cole Parmer 092–04 rotameter (for flow rates up to 2.3 standard liters per minute (SLM)), or by an Omega FMA–A2310 mass flow meter (for flow rates up to 12 SLM), as shown in figure 1(b), both connected to the gas supply line of 1/4 inch in diameter. Most of these experiments are conducted at a buffer gas flow rate ranging from 0.1–2.0 SLM, although some of the measurements are performed in an isolated cell, without the flow. Operating at high buffer gas flow rates produces rapid evaporative cooling of the liquid, in some cases resulting in ice formation in the distilled water. Pressure in the discharge cell is measured using an MKS 910 pressure gauge, connected to a 1 inch diameter exhaust line downstream of the cell, as shown in figure 1(b). In these experiments, test section pressure is varied between 5 Torr and 100 Torr. The flow is maintained by a Stokes 10 cfm vacuum pump.

A custom-made capacitive probe, described in greater detail in our previous work [19, 20], is placed above the quartz test cell filled with nitrogen at 20 Torr and a flow rate of 0.2 SLM, positive pulse polarity.

‘top view’ image of the plasma, the top Teflon plate and the capacitive probe are removed and replaced by a mirror placed at a 45° angle, such that both images are taken by the camera at the same time. The camera gate timing is controlled by a Stanford Research Systems DG645 digital delay generator, using the high-voltage pulse produced by the plasma generator as a ‘master clock’.

To detect the plasma chemical reaction products that may be produced in a surface ionization wave discharge over a liquid–vapor interface, the discharge is operated in a previously evacuated, isolated cell, without the buffer gas flow, i.e. in a saturated vapor above the liquid surface. After operating the discharge for 5–10 min, the mixture of reactants and products is sampled into a previously evacuated glass absorption cell 20 cm long, with two CaF2 windows at the ends, as shown in figure 1(b). The absorption cell is then placed into the absorption port of a Varian 660-IR FTIR spectrometer, and absorption spectra are taken with a spectral resolution of 0.25 cm⁻¹, over a spectral range of 700–6000 cm⁻¹. To verify that the species detected in the FTIR absorption spectra indeed originated from the discharge over the liquid–vapor interface, a set of four spectra is taken each time: (1) and (2) are spectra of samples from the test section filled only with the buffer gas (i.e. without the liquid and vapor) with and without the discharge; (3) and (4) are spectra of samples taken from the test section filled with liquid, at approximately the same vapor pressure as in cases (1) and (2), with and without the discharge.

3. Results and discussion

Figures 2 and 3 show the positive and negative polarity pulse voltage, current and coupled energy waveforms for the surface ionization wave discharge propagating along the bottom wall of the quartz test cell filled with nitrogen at 20 Torr and a flow rate of 0.2 SLM, at pulse repetition rate of 200 Hz. Since the pulser generates alternating positive and negative polarity pulses, taking the data in the negative polarity discharge was performed simply by triggering the probes (high-voltage,
Figure 3. Pulse voltage, current and coupled energy waveforms in the surface ionization wave discharge propagating over a quartz surface in nitrogen. $P = 20$ Torr, $N_2$ flow rate 0.2 SLM, negative pulse polarity.

Figure 4. Capacitive probe traces for a positive polarity surface ionization wave discharge, taken at different axial locations along the discharge cell, 10 mm apart, under the conditions of figure 2. Also shown is the applied voltage pulse, plotted on the same time scale.

Figure 5. Capacitive probe traces for a negative polarity surface ionization wave discharge, taken at different axial locations along the discharge cell, 10 mm apart, under the conditions of figure 3. Also shown is the applied voltage pulse, plotted on the same time scale.

Figure 6. Trajectory of the positive polarity surface ionization wave over a quartz surface, under the conditions of figure 2. Wave speed is determined from the slope of the trajectory.

Figure 7. Trajectory of the negative polarity surface ionization wave over a quartz surface under the conditions of figure 3. Wave speed is determined from the slope of the trajectory.

current and capacitive), as well as the camera, on the negative pulses. Under these conditions, the positive polarity pulse peak voltage and current are approximately 11 kV and 10.5 A, voltage pulse FWHM is about 100 ns, and coupled energy is about 4.0 mJ/pulse. Although the peak voltage for the negative polarity pulse is higher (13 kV versus 11 kV), both peak current (8.5 A) and coupled pulse energy (2.6 mJ/pulse) are lower than the respective parameters for the positive polarity discharge.

Figures 4 and 5 show capacitive probe signals at different axial locations 1 cm apart, along with the applied pulse voltage waveform, plotted on the same time scale. The capacitive probe signal is very reproducible pulse-to-pulse, with an amplitude jitter of $\sim 0.1$ V ($\sim 2\%$) and a time jitter of $\sim 1$ ns. It can be seen that the ionization wave starts when the pulse voltage is rising and continues to propagate along the channel when the voltage peaks and decays, although at a gradually decreasing speed. The wave arrival time at a given axial location is defined as the moment when the capacitive probe signal peaks. Figures 6 and 7 show positive and negative polarity wave $x$–$t$ trajectories, plotted together with the voltage pulse shape. As mentioned in section 2, the left-most position of the capacitive probe ($x = 0$ in figures 6 and 7) is 50 mm from the tip of the high-voltage electrode. From figure 6, it can be seen that the positive polarity wave speed, defined as
the trajectory slope, decreases from $V = 0.20 \text{ cm ns}^{-1}$ in the region closer to the high-voltage electrode to approximately $V = 0.05 \text{ cm ns}^{-1}$ as the applied voltage decreases and as the wave moves closer to the grounded electrode. The distance over which the wave propagates is approximately 20 cm (see figure 6). The negative polarity wave speed decreases much faster along the channel, from $V = 0.16 \text{ cm ns}^{-1}$ to $V = 0.04 \text{ cm ns}^{-1}$ over only about 10 cm, compared to about 20 cm for the positive polarity wave.

ICCD images of the positive and negative polarity surface ionization wave discharges (side view and top view) under the conditions of figures 2 and 3 are shown in figures 8 and 9 for two moments of time separated by 40 ns. It can be seen that the wave indeed propagates near the bottom wall of the test section, the wave front appears nearly straight and the plasma emission behind the wave front is diffuse and nearly uniform. The wave speed calculated from the difference in the wave front locations in these images is consistent with the capacitive probe data shown in figures 6 and 7.

From figures 6 and 7, it is evident that in the channel accessible to the capacitive probe, the wave is propagating during the late rise and the subsequent fall of the high-voltage pulse. Analysis of the pulse current waveforms shows that the electric charge is accumulated on the dielectric surfaces during the voltage rise, i.e. when $d |U|/dt > 0$, with some of it removed back to the external circuit during the voltage fall ($d |U|/dt < 0$) and after the pulse, as illustrated in figures 10 and 11. In the nitrogen plasma over the quartz surface, the surface charge decays nearly exponentially after the discharge pulse, with a characteristic decay time of $\tau \approx 0.26 \mu\text{s}$ for positive polarity and $\tau \approx 0.21 \mu\text{s}$ for negative polarity pulses (see figures 10 and 11). The residual surface charge may also be neutralized by the subsequent opposite polarity pulse. If no additional surface charge removal occurs for delay times after the pulse of $\sim 1 \mu\text{s}$ and longer, the estimated upper bound values of positive and negative charge accumulated on the surface during the pulses are $q_{\text{pos}} = 0.45-0.65 \mu\text{C}$ and $q_{\text{neg}} = 0.43-0.48 \mu\text{C}$ (see figure 10 and 11), suggesting a non-zero time-averaged negative charge of $\bar{|q_{\text{neg}}|} \approx 0.1 \mu\text{C}$.

To provide qualitative insight into the surface ionization wave behavior, the results of figures 3 and 7 are compared with the predictions of a self-similar solution for a surface ionization wave propagating with constant speed, discussed in detail in [17, 21]. Briefly, the model predicts near-wall distributions of axial and transverse electric field components, electron density and surface plasma sheet thickness along the wave. The
constant wave speed, \( V \), dielectric thickness and permittivity, \( d \) and \( \varepsilon \), as well as pressure, \( P \), Townsend ionization coefficient, \( \alpha(E/P) \) and electron mobility, \( \mu_e \), are the input parameters of the model, while the rate of voltage rise on the high-voltage electrode necessary to sustain the wave, \( dU/dt \), wave propagation distance, \( L(t) = Vt \), and the plasma sheet thickness, \( \delta \), are the predicted parameters. The electron density ahead of the wave, assumed to be very low, \( n_e = 10^4 \text{ cm}^{-3} \), has a fairly weak effect on the model predictions. The model is expected to be in qualitative agreement with the data presented here during the rising part of the voltage pulse, when the ionization wave speed is approximately constant (see figures 3 and 7). However, quantitative analysis of ionization wave propagation during the falling part of the pulse (such as that occurring under the conditions of this study, see figures 3 and 7), where a self-similar solution is not available, requires kinetic modeling.

The results for the negative polarity wave, propagating in nitrogen at \( P = 20 \text{ Torr} \) over a quartz wall \( d_Q = 1.75 \text{ mm} \) thick (\( \varepsilon_Q = 3.8 \)) at \( V = 0.15 \text{ cm ns}^{-1} \), are plotted in figures 12–14 versus the self-similar variable, \( \xi = x + Vt \). Under these conditions, the predicted voltage rise rate is nearly constant, \( dU/dt = 0.22 \text{ kV ns}^{-1} \) (voltage rise time from zero to \( U = 12 \text{ kV} \) is \( \tau_{\text{pulse}} = 52 \text{ ns} \)), consistent with the experimental value for the negative pulse of \( (dU/dt)_{\text{max}} \approx 0.24 \text{ kV ns}^{-1} \) (see figure 3). From figure 12, it can be seen that, as expected, the electric field in the wave front is dominated by transverse field, \( E_y \), enhanced by a thin dielectric layer with a relatively high \( \varepsilon \). Breakdown in the wave front, beginning at peak reduced electric field of \( E/P \approx 650 \text{ V cm}^{-1} \text{ Torr}^{-1} \) (\( E/P \approx 2000 \text{ Td} \)), produces rapid axial charge separation and charge accumulation on the dielectric surface, resulting in plasma self-shielding and reduction of both electric field components (see figure 12). The thickness of the plasma layer, predicted by the model, \( \delta \approx 500 \mu \text{m} \), is determined from matching the transverse current integral over the space charge region in the wave front (where \( \rho = 0 \) and the axial current behind the wave front \( [21], \int_{\rho=0}^{\rho=\delta} j_y(y=0)dx + \int_{0}^{\infty} j_x(y)dy \big|_{\rho=0} = 0 \) (see figure 12). The electric field behind the wave front, on the other hand, is dominated by the axial field (see figure 12), which needs to remain sufficiently high, \( E_x/P \approx 50–100 \text{ V cm}^{-1} \text{ Torr}^{-1} \) (\( E_x/N \approx 150–300 \text{ Td} \)), to provide additional ionization, sustain the current to the dielectric surface, and keep increasing its potential as the voltage on the electrode continues to increase. Thus, the axial current at any location in the wave, \( I_x(\xi^+) \), is the same as the transverse current integral over the interval between the wave
front and \( \xi^* \), \( I_x(\xi^*) = \int_0^{\xi^*} j_y(\xi) d\xi \) (see figure 13). By the time the voltage on the electrode reaches \( U = 12 \text{ kV} \), the wave propagates over approximately \( L = 9 \text{ cm} \), consistent with the experimental observations (see figure 7). From figure 13, it can also be seen that ionization in the plasma sheet behind the wave front, several centimeters long, considerably exceeds ionization in the wave front, increasing the electron density by over an order of magnitude. Because of this, most of the energy is coupled to the plasma behind the ionization wave front (see figure 14). In the self-similar ionization wave solution, the energy stored due to charge accumulation on the dielectric surface is equal to the energy dissipated in the plasma as Joule heat, \( Q_{\text{coupled}} = Q_{\text{stored}} \). The total predicted coupled/stored energy when the voltage reaches \( U = 12 \text{ kV} \) is \( Q = Q_{\text{coupled}} + Q_{\text{stored}} = 0.9 \text{ mJ/cm} \) of channel width (see figure 14), i.e. \( QW = 2.25 \text{ mJ/pulse} \), close to the experimental value of \( 2.6 \text{ mJ/pulse} \) measured for the entire pulse (see figure 3). Finally, charge stored by the wave on the dielectric surface during the voltage rise, predicted by the model, is \( q = -0.23 \mu \text{C} \), consistent with peak experimental charge (current integral over time) stored in the load, \( q_{\text{load}} \approx -0.45 \mu \text{C} \).

Extending the current model predictions to the positive polarity voltage pulse requires knowing the effective emission coefficient from the dielectric (quartz or water) surface, \( \gamma_{\text{eff}} \), which is highly uncertain and may strongly depend on transverse electric field [22], as well as on the surface charge density. If \( \gamma_{\text{eff}} \ll 1 \), this would result in an extremely high transverse electric field on the dielectric surface, \( E_y \approx U/\delta \approx 10^4 \text{ kV/cm} \) \( (E/N \approx 10^4 \text{ Td}) \). This is inconsistent with the significant peak positive charge accumulated on the surface, \( q_{\text{pos}} \approx 0.45 \mu \text{C} \) (see figure 10), which indicates efficient electron emission from the dielectric surface during the positive polarity pulse. On the other hand, if \( \gamma_{\text{eff}} \approx 1 \), such that electron emission from the dielectric surface does not limit the current in the positive polarity discharge, transverse electric field would be very low, similar to the negative polarity wave (see figure 12). This assumption, however, results in the model predictions (in particular, wave speed \( V \) and propagation distance \( L \)) being nearly identical to the negative polarity results for the same \( dU/dt \), shown in figures 12–14. However, in the current experiments a significant difference between the two wave polarities was observed, with the distance traveled by the positive polarity wave being greater by up to a factor of two (compare figures 6 and 7). This indicates that an intermediate case is realized, such that a near-surface transverse electric field is present behind the positive ionization wave front, but is largely absent in the negative polarity wave.

The transverse electric field in the positive polarity wave under the current conditions can be estimated from the difference observed between the negative and positive polarity wave speed, as follows. In a constant-speed surface ionization wave, the key parameter controlling the wave speed and the wave propagation distance is the axial field in the plasma sheet behind the wave, since \( dU/dt = E_y V \approx \text{const} \). Thus, increasing the average wave speed for the same rate of voltage increase on the high-voltage electrode would require reduction of the axial field in the plasma sheet, \( E_y \), by approximately a factor of two to double the wave propagation distance. Since ionization behind the negative polarity wave front is sustained primarily by the axial field (see figure 12), its significant reduction in the positive polarity wave would only be possible if a comparable ionization rate is generated by the transverse field accelerating the electrons extracted from the dielectric surface. The magnitude of the transverse field required can be estimated by setting the rate of ionization by the transverse field in the positive polarity wave to be of the same order as the rate of ionization by the axial field in the negative polarity wave, as follows,

\[
\alpha(E_y)\mu_e E_y = A \exp \left( -\frac{B}{E_y/P} \right) \mu_e E_y \approx \alpha(E_y) V
\]

\[
= A \exp \left( -\frac{B}{E_y/P} \right) V . \tag{1}
\]
For $B = 342 \text{ V cm}^{-1} \text{Torr}^{-1}$, $\mu_e P \approx 3 \times 10^5 \text{ cm}^2 \text{Torr}^{-1} \text{s}^{-1}$ [23], and $E_x/P \approx (dU/dt)/VP \approx 70 \text{ V cm}^{-1} \text{Torr}^{-1}$ in the negative polarity wave, the transverse field in the positive polarity wave is $E_y/P \approx 300 \text{ V cm}^{-1} \text{Torr}^{-1}$ ($E_y/P \approx 1000 \text{Td}$), $E_y \approx 6 \text{kV cm}^{-1}$ and the potential difference between the plasma sheet and the dielectric surface is $\Delta \phi \approx E_y \delta \approx 300 \text{ V}$. This estimate provides a lower bound of $E_y$ in the positive polarity wave, for the effective secondary electron emission coefficient of $\gamma_{\text{eff}} \approx \exp[\alpha (E_y \delta)] - 1 \approx 0.3$. Lower values of $\gamma_{\text{eff}}$ would result in higher estimated transverse field values.

Figures 15 and 16 show plasma emission images for positive and negative polarity surface ionization wave discharges propagating over a distilled water surface, for the same buffer gas at the same pressure and flow rate (nitrogen at 20 Torr and 0.2 SLM) and a pulse repetition rate of 500 Hz. Comparison of pulse wave forms, as well as wave $x$–$t$ trajectories, demonstrate close similarity between the surface ionization waves propagating over a quartz wall and over a water surface. Specifically, pulse peak voltage, current and coupled energy, as well as wave speed are very close to each other, although the plasma emission intensity distributions over the water surface are somewhat less uniform compared to the surface discharge over the quartz wall (see figures 8 and 9). Note that, unlike in the discharge over the quartz surface, significant charge accumulation on the water surface was detected up to $\sim 1 \mu \text{s}$ after the pulse, both for positive and negative polarity, $q_{\text{pos}} \approx 0.3 \mu \text{C}$ and $|q_{\text{neg}}| \approx 0.2 \mu \text{C}$ (see figures 10 and 11). However, no detectable motion of the liquid, such as water surface deformation by strong dc electric fields [24], was observed during the current experiments. This suggests little net charge accumulation on the liquid surface on the long time scale, due to either neutralization of surface charge by opposite polarity pulses or slower surface charge removal between the pulses. As can be seen, the discharge predominantly propagates along the water surface and little emission is detected near the top wall of the test section (see figures 15 and 16).

Measurements taken over the water surface at different nitrogen buffer flow rates, from 0.1–1.0 SLM, did not show a significant effect of the flow rate on the surface discharge parameters, as expected. Indeed, at these conditions, the Reynolds number based on the channel hydraulic diameter, $\Delta = 2WH/(W + H) \approx 3 \text{ cm}$, is $Re_{\Delta} \approx 2.5–25$, $Pr \approx 0.7$, and the flow in the channel can be assumed to be fully developed, $(x/\Delta)_{\text{ch}} \approx 0.06 \times Re_{\Delta} \times Pr \approx 0.1–1 \ll L/\Delta \approx 7$, such that the Sherwood number for convection mass transfer is [25]

$$Sh_{\Delta} = \frac{h\Delta}{D} = \frac{\delta_y}{\rho_{\text{surface}} - \rho_{\infty}} \approx 3.0.$$  \hspace{1cm} (2)

In (2), $D \approx 0.25 \text{ cm}^2 \text{s}^{-1} \times (760/P(\text{Torr})) \approx 9.5 \text{ cm}^2 \text{s}^{-1}$ is the water vapor diffusion coefficient, $\rho_{\text{surface}} = \rho_{\text{sat}} \approx 9-17 \mu \text{g cm}^{-3}$ is the saturated water vapor density on the liquid surface at $T = 10–20^\circ\text{C}$, $\rho_{\infty} \approx 0$ is the lower bound for water vapor density away from the liquid surface, and
\[ h = \frac{\dot{m}_w}{(\rho_{\text{surface}} - \rho_m) = D \times \left(\frac{d\rho}{dy}\right)_{\text{surface}}/(\rho_{\text{surface}} - \rho_m)} \approx 9.5 \text{ cm s}^{-1} \text{ is the convection mass transfer coefficient.} \]

From (2), the upper bound of water vapor concentration variation across the near-surface plasma sheet \( \delta = 0.5 \text{ mm thick is } \left(\rho_{\text{sat}} - \rho_{\text{vap}}\right)/\left(\rho_{\text{sat}} - \rho_m\right) \approx 0.01 \ll 1 \). Note that saturated water vapor pressure at \( T = 10-20^\circ \text{C}, \ P_{\text{sat}} = 9.2-17.4 \text{ Torr}, \) is fairly close to the buffer nitrogen flow pressure of \( P = P_{\text{sat}} = 9.220 \text{ Torr} \). Thus, under the current conditions the surface ionization wave discharge propagates essentially in a mixture of saturated water vapor with nitrogen.

In a fully developed flow, the mass flow rate of evaporation from the liquid water surface is determined as

\[ \dot{m}_w = \rho_{\text{sat}} u_m W H \left[ 1 - \exp\left( -\frac{L h}{u_m H}\right) \right], \quad (3) \]

where \( u_m \) is the mean flow velocity and the exponential factor accounts for the increase in the mean water vapor concentration, \( \rho_m \), along the channel, from \( \rho_m = 0 \) at the entrance to the asymptotic value of \( \rho_m \to \rho_{\text{sat}} \approx 9-17 \mu \text{g cm}^{-3} \) at \( t_{\text{diff}} \sim H/h \gg \tau_{\text{conv}} L/u_m \). For the buffer flow rate of 0.1 SLM (\( u_m \approx 6 \text{ cm s}^{-1} \)), this gives \( \dot{m}_w \approx 0.5-1.0 \text{ mg s}^{-1} \) and a rate of heat removal from the surface of \( \dot{Q} = \dot{m}_w \Delta h_{\text{vap}} \approx 1-2 \text{ W}, \) where \( \Delta h_{\text{vap}} = 2.26 \text{ kJ g}^{-1} \) is the latent heat of vaporization. At 1 SLM, (3) gives \( \dot{m}_w \approx 2.5-5.0 \text{ mg s}^{-1} \) and \( \dot{Q} \approx 5-10 \text{ W}. \) At high buffer gas flow rates, above \( \approx 10 \text{ SLM } (R \Delta \approx 250, \ (x/\Delta)_{11} \approx 10, \ L/\Delta \approx 7), \) the flow is no longer fully developed, mass transfer can be estimated from the laminar ‘combined entry’ flow Sherwood number correlation \[ S_{\text{Sh}} = \frac{\bar{h} \Delta}{D} \approx 1.86 \left( \frac{R \Delta \chi}{L/\Delta} \right)^{1/3}, \quad (4) \]

\( Sc = 0.7, \) which gives \( S_{\text{Sh}} \approx 5.4, \ h \approx 17 \text{ cm s}^{-1}, \dot{m}_w \approx \bar{h} \rho_{\text{sat}} W L \approx 7-15 \text{ mg s}^{-1} \) and \( \dot{Q} \approx 15-30 \text{ W}. \) If the channel wall is maintained at room temperature, \( T \approx 20^\circ \text{C}, \) water surface temperature reduction can be estimated as \( \Delta T = \frac{\theta_{\text{th}}}{k_w} W L, \) where \( \theta_{\text{th}} \approx 5 \text{ mm} \) and \( k_w = 0.6 \text{ W m}^{-1} \text{K} \) are the depth and the thermal conductivity of water, \( \Delta T \approx 3 \text{ °C} \) at 0.1 SLM, \( \Delta T \approx 10 \text{ °C} \) at 1 SLM, and \( \Delta T \approx 20 \text{ °C} \) at 10 SLM. Thus, operating at high buffer flow rates may require heating of the liquid surface by the discharge or using an external heater to prevent rapid evaporative cooling and ice formation. Since the coupled discharge energy at these conditions is \( \dot{Q} \approx 3.5-5.0 \text{ mJ/pulse}, \) at 0.2 SLM the surface discharge can be operated at steady-state, near room temperature liquid surface conditions at a pulse repetition rate of \( \approx 0.5-1.0 \text{ kHz}. \)

Similar to surface ionization wave discharge in nitrogen propagating over the quartz surface, ionization behind the negative polarity wave front in water vapor is sustained by the axial electric field. In this case, due to the strong electron affinity of water vapor, the difference between the ionization coefficient and electron attachment coefficient, \( \alpha (E) / (N) - \eta (E) / (N) > 0, \) needs to be sufficiently high to sustain the current to the liquid surface as its potential is increasing. Recent measurements of the effective ionization coefficient in water vapor, \( \alpha - \eta [22], \) show that the lower bound axial reduced electric field in the negative polarity surface ionization wave pure water vapor is \( (E / N)_{\text{min}} \approx 130 \text{Td} \) \( (E / (\Delta P) \approx 40 \text{ V cm}^{-1} \text{ mm}^{-1}). \) Similar to the results in nitrogen over the quartz surface, the average speed and propagation distance of a positive polarity ionization wave in water vapor are greater compared to the negative polarity wave, suggesting the presence of a significant transverse electric field near the liquid surface. For an ionization wave in pure saturated water vapor over a liquid water surface at \( P = 20 \text{ Torr}, \) the kinetic model using the effective ionization coefficient, \( \alpha - \eta, \) and the electron drift velocity from [22], predicts a higher wave speed and propagation distance compared to the wave in nitrogen over quartz at the same pressure and the same voltage rise rate of \( dU / dt = 0.22 \text{ kV ns}^{-1}, \ V = 0.21 \text{ cm ns}^{-1} \) compared to \( V = 0.17 \text{ cm ns}^{-1}. \)

Figures 17 and 18 show plasma emission images taken in positive and negative polarity ionization wave discharges over a 1-butanol surface, with nitrogen buffer at \( P = 20 \text{ Torr} \) and 0.1 SLM, at a pulse repetition rate of 500 Hz. As discussed above, at these conditions the surface ionization wave propagates in a mixture of saturated butanol vapor with nitrogen. Again, the discharge parameters remain fairly close to the ones measured without the liquid and with distilled water in the test cell. It can be seen that in the cell with liquid butanol, a somewhat weaker ionization wave also propagates over the top surface of the test cell. This is likely to be due to the lower dielectric constant of butanol.
1-butanol compared to that of water, $\varepsilon_B = 17.8$ versus $\varepsilon_W = 78.5$, which results in a lower electric field over the liquid butanol surface compared to the water or quartz surface, by a factor of $\sim (d_Q/\varepsilon_Q + d_B/\varepsilon_B) / (d_Q/\varepsilon_Q + d_W/\varepsilon_W) \approx (d_Q/\varepsilon_Q + d_B/\varepsilon_B) / (d_Q/\varepsilon_Q) \approx 1.5$, i.e. by about 50%. This fact, combined with the higher Townsend ionization coefficient in butanol vapor compared to nitrogen and water vapor at high reduced electric field values, $E/P > 200$ V cm$^{-1}$ Torr$^{-1}$ [22, 23, 26], may explain the presence of the second wave. Basically, at these conditions the field near both top and bottom surfaces may be sufficient to produce ionization and sustain the wave.

The comparison of surface ionization wave speed over butanol, distilled water and quartz, shown in figure 19, shows that wave speed over butanol is somewhat higher, both for the positive and negative polarities. The maximum and minimum wave speeds for these three cases, determined from the slopes of $x$–$t$ diagrams, are summarized in table 1. Also, the wave over the butanol surface was observed to propagate over a longer distance from the high-voltage electrode, all the way to the grounded electrode, producing readily detectable visible emission near the grounded electrode which was not observed in the surface discharges over the quartz wall or distilled water surface. This shows that a direct current path was established between the high-voltage electrode and the grounded electrode during the discharge pulse. For all three sets of conditions (discharge over the quartz wall, distilled water surface and butanol surface), both ionization wave speed and the distance over which the wave propagated were observed to decrease when buffer gas pressure was increased from $P = 20$ Torr to 40 Torr. However, the surface ionization wave was still detected at nitrogen buffer pressures of up to $P = 60$ Torr and at helium buffer pressures of up to $P = 160$ Torr.

Shutting off the N$_2$ buffer gas flow, i.e. first closing valve 2 in figure 1(b), while keeping the vacuum pump running to evacuate the test cell to $P \sim 0.2$ Torr, and then closing valve 4, resulted in test cell pressure reaching close to saturated vapor pressure ($P_{sat} = 4.8$ Torr for 1-butanol and $P_{sat} = 17.5$ Torr for water at $T = 20^\circ$C). Under these conditions, the surface ionization discharge was still observed to propagate over the liquid–vapor interface, in both butanol and water. In butanol, shutting off the nitrogen buffer flow and operating in saturated vapor resulted in a significant increase of pulse peak current and coupled pulse energy, from 4.0 to 8.0 mJ/pulse (for positive polarity) and from 3.5 to 8.5 mJ/pulse (for negative polarity). Ionization wave speed also increased, reaching peak values of $V = 0.4$ cm ns$^{-1}$ and $V = 0.5$ cm ns$^{-1}$ for the positive and negative polarity waves, respectively, and remained nearly constant along the discharge channel, $V \approx 0.27$ cm ns$^{-1}$, for both polarities (see figure 20). Under these conditions, the ionization wave propagates in the channel during both voltage increase and reduction, as can be seen from figure 20. The much less significant difference between the positive and the negative polarity wave speeds in saturated butanol vapor, at $P \approx 5$ Torr, compared to the results obtained at a higher pressure of $P = 20$ Torr, is typical for volumetric ionization waves, as observed previously in nitrogen and helium [19, 20]. Under these conditions, ICCD images have not been taken, so it remains uncertain whether the surface wave under these conditions still predominantly propagates over the liquid–vapor interface, or if the wave developing over the top wall of the test section and volumetric plasma become more pronounced. For the surface ionization wave in saturated butanol vapor over a liquid butanol surface at $P = 5$ Torr, the kinetic model using the ionization coefficient for butanol from [25] predicts a wave speed and propagation distance consistent with the experimental results for the voltage rise rate of $dU/dt = 0.22$ kV ns$^{-1}$, $V = 0.40$ cm ns$^{-1}$ and $L = 21$ cm. However, the predicted coupled pulse energy is only 3.4 mJ ($Q = 1.5$ mJ per 1 cm of channel width), considerably lower than that measured, suggesting that in the experiments the plasma may indeed extend over the top and side walls of the channel and thus cover a larger surface area.

Using high-voltage diodes to selectively block positive or negative polarity pulses generated by the alternating polarity high-voltage power supply (see section 2), such that only half of the output pulses were applied to the high-voltage electrode, resulted in higher pulse peak voltage and therefore higher coupled pulse energy (by up to 30%) and ionization wave speed. However, the coupled pulse energy increase was not as significant as the nearly 50% reduction of time-averaged coupled discharge power caused by blocking half of the output pulse.
trajectories over the butanol surface, in saturated butanol vapor. 

...transient increase of emission at the liquid layer and the electrodes (see figure 1). Conducting decaying surface plasma channel remains between pulses, 2–5 ms under the current conditions, if a sufficiently well leak to the electrodes during the time delay between the pulses. A comparable increase of the coupled energy can result in higher output pulse peak voltage. The motivation also be achieved by increasing input dc voltage, which would result in higher output pulse peak voltage. The motivation for the use of an alternating polarity pulse generator was to reduce the effect of net charge accumulation on the liquid surface layer or due to the finite conductivity of the surface plasma layer. This suggests that surface charge accumulated during the pulse leads to electrical breakdown between the surface and the grounded electrode in the afterglow, resulting in charge removal on a microsecond time scale.

To determine whether ionization wave discharges on a liquid butanol surface may induce plasma chemical reactions, the reaction products were analyzed using FTIR absorption spectroscopy. FTIR absorption spectra of plasma chemical reaction products accumulated in the discharge were taken by sampling the products from the cell filled with liquid butanol/saturated butanol vapor, with and without a ionization wave discharge operated at the liquid–vapor interface at a pulse repetition rate of 500 Hz (conditions of figure 20), over 10 min. The results are shown in figure 21. It can be seen that both absorption spectra, taken with and without the discharge, exhibit the presence of butanol vapor (C₅H₉OH) and water vapor, which is likely to be present in liquid butanol. However, the spectrum taken after operating the discharge also shows the presence of plasma chemical reaction products, including carbon monoxide (CO), methane (CH₄), acetylene (C₂H₂), ethane (C₂H₆), propane (C₃H₈), formaldehyde (CH₂O), methanol (CH₃OH) and possibly acetaldehyde (CH₃CHO). These species have been identified by comparison with the synthetic spectra calculated HITRAN database [27]. In particular, the significant absorbance increase near 2850–3000 cm⁻¹ in the spectrum of plasma chemical reaction products, near one of the butanol absorption bands (see figure 21), is caused primarily by its conversion to propane, rather than by an increase of butanol vapor in the products. Indeed, the partial pressure of butanol vapor, which is controlled mainly by the temperature in the discharge cell, remains approximately the same, as indicated by the weak change of absorbance on other butanol bands, near 1000–1100 cm⁻¹ and 3600–3700 cm⁻¹. The absolute number densities of reaction products and their specific energy cost can be calculated from these spectra using calibration gas mixtures as well as the HITRAN synthetic spectra, as has been done in our previous work [28, 29]. The preliminary estimate of CO partial pressure in the absorption cell, based on FTIR calibration spectra taken using known amounts of CO, is P_CO = 1.25 Torr, i.e. the CO mole fraction in the mixture at these conditions is approximately 9%.

**4. Summary**

Surface ionization wave discharges generated by high-voltage nanosecond pulses, propagating over a quartz surface and

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### Table 1. Maximum and minimum ionization wave speeds over different surfaces. Nitrogen buffer, \( P = 20 \) Torr, flow rates 0.2 SLM (quartz, water) and 0.1 SLM (butanol).

<table>
<thead>
<tr>
<th>Case</th>
<th>Quartz</th>
<th>Water</th>
<th>Butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Positive</td>
<td>Negative</td>
<td>Positive</td>
</tr>
<tr>
<td>( V_{\text{max}}, \text{ cm ns}^{-1} )</td>
<td>0.20</td>
<td>0.16</td>
<td>0.17</td>
</tr>
<tr>
<td>( V_{\text{min}}, \text{ cm ns}^{-1} )</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>

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**Figure 20.** Positive and negative polarity surface ionization wave trajectories over the butanol surface, in saturated butanol vapor. \( P_{\text{atm}} = 5 \) Torr, repetition rate 500 Hz. Red symbols: positive polarity wave; blue symbols: negative polarity wave. The wave speed on the linear part of the trajectory is approximately 0.27 cm ns⁻¹.
dielectric liquid surfaces (distilled water and 1-butanol) have been studied in a rectangular cross section channel. The ionization wave discharge was initiated using a custom-made, alternating polarity, high-voltage nanosecond pulse plasma generator, operated at a pulse repetition rate of 100–500 Hz. In these experiments, the pulse peak voltage and current were in the range of 10–15 kV and 7–20 A, respectively, the pulse FWHM was approximately 100 ns and the coupled pulse energy was 2–9 mJ/pulse. The surface ionization wave propagation was detected and the wave speed was measured using a capacitive probe. Nanosecond gate ICCD camera images demonstrated that the ionization wave was propagating predominantly over the quartz surface or liquid surface adjacent to the grounded waveguide placed on the bottom wall of the test cell, although in some cases a weaker plasma emission was also detected near the top test section wall. Under all experimental conditions tested, the surface plasma ‘sheet’ was diffuse and fairly uniform, both for positive and negative polarities. The parameters of ionization wave discharge propagating over the distilled water surface (coupled pulse energy, wave speed and appearance of the plasma) are close to those of the discharge over a quartz wall. No perturbation of the liquid surface was detected. In most cases, the positive polarity surface ionization wave tended to propagate at a higher speed and over a longer distance compared to the negative polarity wave.

A diffuse, highly reproducible surface ionization wave discharge was also observed over the liquid butanol–saturated vapor butanol interface, at \( P = 5 \) Torr, as well as over the distilled water–saturated water vapor interface, at \( P = 20 \) Torr, without the buffer gas flow. In the butanol–butanol vapor, the wave speed was higher than in the butanol–nitrogen buffer flow at \( P = 20 \) Torr, and did not decrease as rapidly. For all three sets of experiments (surface ionization wave discharge over quartz, water and butanol), wave speed and wave distance decreased with pressure. No significant difference was detected between the surface ionization discharges sustained using single-polarity (positive or negative) or alternating polarity high-voltage pulses. The plasma emission images yield preliminary evidence of charge removal from the liquid surface in the afterglow between the pulses on a microsecond time scale. Products of the plasma chemical reaction accumulated in the ionization wave discharge over the liquid butanol–saturated butanol vapor, without the buffer flow, were detected ex situ using FTIR absorption spectroscopy. Reaction products include CO, alkanes (CH\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_8\)), alkenes (C\(_2\)H\(_2\)), aldehydes (CH\(_2\)O) and lighter alcohols (CH\(_3\)OH).

The basic phenomena controlling the propagation of nanosecond pulse surface ionization waves over liquid dielectrics studied in this work appear qualitatively similar to those in surface streamers over solid dielectrics (see e.g. [30]). They include electric field enhancement near the dielectric surface, as well as surface charge deposition/removal. In liquid dielectrics, the latter effect is also affected by the electrical conductivity of the liquid. The effect of negative ions, as discussed in [31], appears to be unlikely under the current conditions, since the wave speed over the water and quartz surfaces (both in a nitrogen buffer) are nearly identical (see figure 19(a)). Indeed, previous experiments in low-pressure volumetric ionization waves sustained by nanosecond duration pulses in nitrogen and dry air [20] indicated that electron attachment and negative ion kinetics do not play a significant role in ionization wave propagation under these conditions. This most likely occurs due to the relatively high reduced electric field in the wave, such that ionization dominates dissociative attachment, as well as due to the low pressure and short discharge pulse duration, both of which reduce the effect of three-body attachment. The surface streamer discharge propagation speed over solid dielectrics measured in [30] (in the range of \( \sim 0.01–0.1 \) cm ns\(^{-1}\) for \( dU/dt \approx 0.05–0.1 \) kV ns\(^{-1}\) and \( P \sim 0.1–1 \) bar), as well as the trend of discharge speed reduction with pressure, are in qualitative agreement with the results presented here. The main difference is that surface streamers accelerate during their propagation [30], while diffuse surface ionization waves in this work slow down significantly. This difference may be caused by a higher conductivity in the streamer compared to that of the diffuse surface plasma, such that the field ahead of the streamer head.

Figure 21. FTIR absorption spectra of samples taken with and without surface ionization wave discharge operated at the liquid butanol–saturated butanol vapor interface at \( P = 14 \) Torr and a pulse repetition rate of 500 Hz, without buffer gas flow. Accumulation time 10 minutes.
increases as it approaches the grounded electrode [30], or by the applied voltage reduction, before the surface wave reaches the grounded electrode.

Formation of ionization waves that are very well reproduced shot-to-shot and generate diffuse surface plasma is one of the main advantages of studying surface discharges at low pressures. This makes it possible to characterize these discharges in repetitively pulsed experiments. On-going and future work includes measuring the absolute number densities of radicals in gaseous bubbles immersed in liquids.

Acknowledgments

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