I. INTRODUCTION

Photochemical reactions induced by irradiation with ultraviolet (UV) light are utilized in a large variety of applications such as surface cleaning,\textsuperscript{1−5} antiviral and bacterial surface disinfection,\textsuperscript{6} air and water purification,\textsuperscript{10−14} photochemical surface modification,\textsuperscript{15−23} wettablity alteration,\textsuperscript{24−31} material deposition,\textsuperscript{32−38} surface charging,\textsuperscript{39−41} photolithography,\textsuperscript{42,43} and the patterning of self-assembled monolayers.\textsuperscript{31−40} The photopatterning of polymer layers due to photoisomerization reactions of azobenzene groups has been studied intensively.\textsuperscript{44−51}

Chowdhury et al.\textsuperscript{66} reported on experiments regarding UV-induced photopolymerization reactions of aniline films floating on water. Golovin and Volpert\textsuperscript{67,68} studied the Marangoni instability of a thin liquid layer subject to uniform illumination that triggers a reversible photochemical reaction. They performed a linear stability analysis as well as numerical simulations of the evolution equations for the height and reactant concentration profiles. Dun et al. studied the laser-pulse-induced deformation of 50-nm-thick Sb\textsubscript{2}Te\textsubscript{3} films due to a competition between thermocapillary and solutocapillary effects.\textsuperscript{60} A displacement of material out of the laser spot was observed for low powers, whereas material accumulation in the laser spot occurred for higher powers. Verma et al. irradiated polystyrene and poly(methyl methacrylate) layers with intense near-UV radiation at 355 nm, which caused local melting of the polymer. Using various apertures, they were able to induce relief patterns in the polymer films with a single laser pulse (∼100 ns).\textsuperscript{69} Katzenstein et al. studied pattern formation after UV illumination of a solid polymer through a mask and induced Marangoni flows.\textsuperscript{70} A displacement of material out of the laser spot was observed for low powers, whereas material accumulation in the laser spot occurred for higher powers.

Arshad et al. presented a perturbation analysis of a coupled convection-diffusion model for UV-induced polymer surface deformations and achieved good agreement with experimental results using polystyrene layers.\textsuperscript{71,72} Kim et al. used a photosensitizer to enhance the UV-photopatterning effect and concluded that an endoperoxide of the photosensitizer is a critical reaction intermediate.\textsuperscript{74} Adding a photobase generator to a polymer film, Kim et al. demonstrated that UV-induced material redistribution could be directed toward either the irradiated or the nonilluminated regions depending on the mode of exposure using either low-intensity and wavelength-selective or high-intensity and broadband illumination. The authors identified decarboxylation and dehydrogenation reactions as the chemical processes driving the flow.\textsuperscript{75}

In this article, we report on the irradiation of aliphatic, liquid hydrocarbon films on stationary substrates with deep-UV light through a mask (Figure 1a). Because of photochemical reactions, the chemical composition of the liquid and thus its surface tension are altered and become spatially nonuniform. As a consequence, so-called solutocapillary Marangoni flows\textsuperscript{76−98} are induced that redistribute the liquid film. We demonstrate that measuring the liquid deformation is a sensitive means of monitoring minute composition changes. We developed a numerical model that quantitatively reproduces the morphological and dynamical features observed in the experiments. Moreover, we determined self-similar solutions that illustrate the mechanisms governing different stages of the dynamics and their parametric dependence.
Figure 1. (a) Deep-UV radiation from a deuterium lamp is partially blocked by a metal mask and partially transmitted to an aliphatic liquid hydrocarbon film. Because of photochemical reactions, the surface tension increases, which induces flow toward the illuminated regions and the formation of a film thickness maximum underneath the unmasked areas. (b) Example of thin liquid film deformation induced by deep-UV irradiation through a rectangular aperture of dimensions 0.9 × 10 mm² (indicated by the red dashed line). The light and dark optical interference fringes allow monitoring of the film thickness distribution. Initial film thickness \( h_0 = 4.8 \) μm. Image height 4.5 mm.

thermal conductivity of \( k \approx 25 \) W/(m·K), which helps to suppress the potential occurrence of temperature gradients that might mask the effects of concentration gradients.

The viscosity of squalane at 23 °C is \( \mu_{\text{squalane}} = 31.9 \) mPa·s, the surface tension\(^{109}\) is \( \gamma = 28.15 \) mN/m, the density\(^{108}\) is \( \rho = 805 \) kg/m³, and the refractive index is \( n_0 = 1.452 \). The self-diffusion coefficient of squalane\(^{101}\) is \( D_s \approx 3 \times 10^{-11} \) m²/s. Kowert and Watson studied the diffusion of organic solutes in squalane.\(^{102}\)

Deep-UV irradiation was performed with a 30 W deuterium lamp (Newport, model number 63163). The effective source diameter is approximately 0.5 mm and is located approximately 20 mm above the squalane film. The exit window is made from synthetic quartz in order to minimize the absorption of deep-UV radiation. The effective emission wavelengths range approximately from 160 to 400 nm. The lamp output does not exhibit any significant start-up effects for illumination times of less than 1 min. A steady-state value of the intensity is reached within 0.25 s of switching it on, after which the illumination times of less than 1 min. A steady-state value of the intensity is reached within 0.25 s of switching it on, after which the intensity remains constant to within ±2%.

The experiments were performed in either an air environment or a chamber flushed with either dry nitrogen or Ar gas. The aperture consisted of a rectangular slit approximately 1 mm wide and 10 mm long in a 2-mm-thick Al plate. The separation between the underside of the Al plate and the squalane film was approximately 0.5 mm. The effective path length of the deep-UV light from the exit window of the lamp to the surface of the squalane film was approximately 7.5 mm. The illumination time \( t_{\text{UV}} \) was varied between 10 and 60 s. A video of a typical experiment is part of the Supporting Information.

For live visualization of the time evolution of the liquid height profile \( h(x, y, t) \) during and after UV exposure, we used optical interferometry in a transmission geometry. A high-speed camera (Photron SA-4) fitted with protective optical filters, a lens system, and a microscope objective (Leitz Wetzlar NPL 5x, NA = 0.09) was mounted underneath the substrate. Because the camera was blinded by the broadband illumination, we introduced a chopper (Thorlabs, model number MC2000) with its blade (Thorlabs, model number MC1F2) rotating at a frequency of 2 rps. When the illumination was blocked by the blade, interferometry images were recorded using an LED light source (Roithner, center wavelength \( \lambda = 625 \) nm). Figure 1b shows an example of an interference image. The height difference represented by two consecutive constructive or destructive interference fringes corresponds to \( \Delta h_{\text{inter}} = \lambda/(2n_0) \approx 215 \) nm. The total film thickness modulation is then determined by evaluating the number of interference fringes between the maximum and minimum positions indicated by the solid lines in Figure 1b and multiplication by \( \Delta h_{\text{inter}} \).

Interferometry using a single wavelength allows only the determination of changes in film thickness, not absolute values. Therefore, we measured the initial film thickness \( h_0 \) using a home-built spectral reflectance system comprising a spectrometer (Ocean Optics, model USB4000) and a tungsten-halogen broadband light source (Ocean Optics, model LS-1-IL).

III. THEORETICAL MODEL

It is likely that a number of different chemical species result from the reaction. In the following text, however, we account for the photogenerated species by means of a single concentration variable \( c \) and assume that surface tension has a linear dependence

\[
\gamma(c) = \gamma_0 + \frac{\partial \gamma}{\partial c} c
\]

with a constant coefficient of \( \partial \gamma/\partial c > 0 \). This is typically a realistic assumption for nonaqueous systems as long as the total photochemical conversion is low.

Furthermore, we assume that the photoreaction leads to an increase in the photoproduct concentration at a constant rate proportional to the local light intensity. This may occur at the liquid–air interface, \( z = h \), if the absorption depth is small, \( \alpha^{-1} \ll h_0 \) or homogeneously throughout the thickness of the thin liquid film if \( \alpha^{-1} \gg h_0 \). Here, \( \alpha(\lambda) \) is the absorption coefficient of the photochemically active UV radiation. The time scale of the experiments typically ranges from 10 to 600 s, which by far exceeds the diffusive time scale \( h_0^2/D_w \lesssim 0.8 \) s. Consequently, in both cases the concentration distribution can be assumed to be vertically equilibrated. Thus, we need to consider only the height-averaged concentration defined as

\[
C(x, y, t) \equiv \frac{1}{h} \int_0^h c \, dz
\]

which depends only on the lateral coordinates \( x \) and \( y \).

The flow of thin, nonvolatile liquid films is governed by the so-called lubrication equation\(^{103}\)

\[
\frac{\partial h}{\partial t} + \frac{\partial Q_x}{\partial x} + \frac{\partial Q_y}{\partial y} = 0
\]

(3)

where

\[
Q_x = \frac{h^2 \tau_x}{2 \mu} - \frac{h^3 \frac{\partial p}{\partial x}}{3 \mu}
\]

and

\[
Q_y = \frac{h^2 \tau_y}{2 \mu} - \frac{h^3 \frac{\partial p}{\partial y}}{3 \mu}
\]

(4)

are the volumetric flow rates,

\[
\tau_x \equiv \frac{\partial \gamma}{\partial x} = \frac{\partial \gamma}{\partial c} \frac{\partial c}{\partial x} \quad \text{and} \quad \tau_y \equiv \frac{\partial \gamma}{\partial y} = \frac{\partial \gamma}{\partial c} \frac{\partial c}{\partial y}
\]

(5)

are the Marangoni stresses,\(^{86}\) along the \( x \) and \( y \) directions and

\[
p = -\gamma \left( \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right) + \rho g h
\]

(6)

is the augmented pressure, representing capillary and hydrostatic pressure contributions. Here, \( g = 9.81 \text{ m/s}^2 \) is the gravitational acceleration. The terms containing \( \tau_x \) and \( \tau_y \) represent Marangoni fluxes in response to surface tension gradients, which are caused by gradients in concentration \( C \) of the photoproducts owing to eq 1. Generally, the direction of Marangoni flow in thin liquid films is from regions of lower toward regions of higher surface tension. The nonuniform
species distribution that sets up the surface tension gradients, however, changes continuously because of diffusion and convection. Therefore, eq 3 is coupled to a convection–diffusion-reaction equation\textsuperscript{104–106} that governs the dynamics of $C(x, y, t)$

$$
\frac{\partial h}{\partial t} + Q_x \frac{\partial C}{\partial x} + Q_y \frac{\partial C}{\partial y} = R_{\text{react}}(x, y, t) + 

+ \frac{\partial}{\partial x} \left( h D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( h D \frac{\partial C}{\partial y} \right)
$$

The term $R_{\text{react}}(x, y, t)$ is the height-integrated photochemical conversion rate with units of length $x$ concentration/time. We distinguish two different cases: surface-dominated and bulk-dominated reactions. In the case of a bulk-dominated reaction, the conversion occurs essentially uniformly across the film thickness. We set $R_{\text{react}} = hj_{\text{bulk}}I(x, y, t)$, where the factor $h$ stems from the height integration. Here, $j_{\text{bulk}}$ is a constant and $I(x, y, t)$ is the scaled UV intensity distribution on the substrate. This implicitly requires the film to be optically thin ($a_{th} \ll 1$). In the case of a surface-dominated reaction, the conversion occurs only in a thin layer adjacent to the liquid–gas interface. The integration of the reaction rate across the film thickness is therefore independent of $h$, and we set $R_{\text{react}} = j_{\text{surf}}I(x, y, t)$, where $j_{\text{surf}}$ is assumed to be constant. This includes the cases of optically thick films ($a_{th} \gg 1$) and reactions that are truly interface-driven.

In both cases, we assume the reaction rate to be proportional to the light intensity, which is known as the Bunsen–Roscoe law of reciprocity, which holds for many systems.\textsuperscript{107–112} By approximation, the reactant and photoproduct concentrations do not enter into $R_{\text{react}}$ because at low conversion the former essentially remains constant and the latter remains very small. The parameters $j_{\text{bulk}}$ and $j_{\text{surf}}$ contain the intrinsic rate constant of the photochemical reaction. We note that these expressions for $R_{\text{react}}$ with constant parameters $j_{\text{bulk}}$ and $j_{\text{surf}}$ are valid only for conversions far below 100%, which is appropriate for our experiments.

The shape function $I(x, y, t)$ of the UV intensity distribution depends on the beam profile as well as the aperture shape. We assume that it is time-independent during the illumination period of $0 \leq t \leq t_{UV}$ and zero afterward. This means that in the model we neglect the presence of the chopper in the illumination system. Given that the effective illumination frequency is 4 Hz and the time scale of typical experiments by far exceeds 1 s, such a time-averaging procedure is permissible (Supporting Information). We approximated the shape function as

$$
I(x, y, t \geq 0) = \Theta(t_{UV} - t, \Delta t) \times

\Theta \left( \frac{1}{2} w_x - |x|, \frac{1}{2} \Delta h \right) \Theta \left( \frac{1}{2} w_y - |y|, \frac{1}{2} \Delta w \right)
$$

where $\Theta$ denotes a smoothed Heaviside function,\textsuperscript{113} $w_x$ and $w_y$ are the aperture widths in the $x$ and $y$ directions, and $\Delta t = 1 \text{ ms}$.

We solved the set of eqs 3–7 numerically using the finite element software Comsol 3.5a. The dimensions of the computational domain (0 $\leq x \leq L_x$, 0 $\leq y \leq L_y$) are typically 10 times the aperture width. The boundary conditions were chosen as

$$
\frac{\partial h}{\partial x} = 0, \frac{\partial p}{\partial x} = 0 \quad \text{and} \quad \frac{\partial C}{\partial x} = 0
$$

at $x = 0$ and $x = L_x$ and

$$
\frac{\partial h}{\partial y} = 0, \frac{\partial p}{\partial y} = 0, \quad \text{and} \quad \frac{\partial C}{\partial y} = 0
$$

at $y = 0$ and $y = L_y$, all of which represent mirror symmetries. The boundaries at $x = L_x$ and $y = L_y$ are sufficiently remote from the aperture such that the surface deformation does not reach it within the typical duration of an experiment.

The initial conditions are a film of uniform thickness $h(x, y, t = 0) = h_0$ and a uniform photoproduct concentration $C(x, y, t = 0) = 0$.

**IV. RESULTS AND DISCUSSION**

Figure 2a shows a typical intensity profile $I(x)$ corresponding to an infinitely long and 1-mm-wide aperture, i.e., for $w_x \rightarrow \infty$ and $w_y = 1 \text{ mm}$. Figure 2b shows the corresponding film thickness profiles at different times after commencing deep-UV illumination.
irradiation. The initially flat film develops two dimples just outside and two local maxima just inside the illuminated region. As time progresses, the dimples deepen and the maxima grow. At \( t \approx 80 \) s, the two maxima coalesce into a single maximum located at \( x = 0 \). Figure 2b also contains the definitions of various parameters that quantify the film thickness modulation: the maximum film thickness increase \( \Delta h_{\text{max}} \equiv \max [h] - h_0 \), the maximum film thickness reduction \( \Delta h_{\text{min}} \equiv h_0 - \min [h] \), the total film thickness modulation \( \Delta h_{\text{tot}} \equiv |\Delta h_{\text{max}}| + |\Delta h_{\text{min}}| \), and the peak-to-peak film thickness modulation \( \Delta h_{\text{pp}} \).

Figure 2c shows numerical simulations of \( \Delta h_{\text{max}}(t) \) as a function of time. For \( t < t_{\text{UV}} \), we observe to good approximation a power law time dependence of \( \Delta h_{\text{max}} \approx t^{1.57} \) (dashed line). The coalescence of the two maxima at \( t \approx 80 \) s manifests itself in a steeper increase in \( \Delta h_{\text{max}} \). At later times, the rate of increase of \( \Delta h_{\text{max}} \) slows down and a peak is reached, after which \( \Delta h_{\text{max}} \) slowly decreases. This is primarily due to lateral diffusion, which eventually leads to the disappearance of the concentration gradients that drive Marangoni flow.

In Figure 3, we present experimental data for the dependence of the total film thickness modulation \( \Delta h_{\text{tot}} \) on the exposure time \( t_{\text{UV}} \). The film thickness modulation \( \Delta h_{\text{tot}} \) as a function of time for \( h_0 = 3.6 \) \( \mu \)m and three different values of \( t_{\text{UV}} = 10, 20, \) and 40 s. Filled circles correspond to experimental data obtained in a nitrogen atmosphere, and the solid lines correspond to two-dimensional numerical simulations using \( D = 3 \times 10^{-11} \) m²/s, \( w_0 = 0.9 \) mm, \( w_j = 10 \) mm, \( \Delta w = 0.28 \) mm, and \( J_{\text{mol}}(\partial \gamma/\partial C) = 3.6 \times 10^{-11} \) N/s. Open diamonds correspond to experimental data obtained in an air atmosphere for \( t_{\text{UV}} = 60 \) s, and the dotted line corresponds to two-dimensional numerical simulations using \( D = 3 \times 10^{-11} \) m²/s, \( w_0 = 0.9 \) mm, \( w_j = 10 \) mm, \( \Delta w = 0.28 \) mm, and \( J_{\text{mol}}(\partial \gamma/\partial C) = 1.2 \times 10^{-11} \) N/s.

Figure 3. Total film thickness modulation \( \Delta h_{\text{tot}} \) as a function of time for \( h_0 = 3.6 \) \( \mu \)m and three different values of \( t_{\text{UV}} = 10, 20, \) and 40 s. Filled circles correspond to experimental data obtained in a nitrogen atmosphere, and the solid lines correspond to two-dimensional numerical simulations using \( D = 3 \times 10^{-11} \) m²/s, \( w_0 = 0.9 \) mm, \( w_j = 10 \) mm, \( \Delta w = 0.28 \) mm, and \( J_{\text{mol}}(\partial \gamma/\partial C) = 3.6 \times 10^{-11} \) N/s. Open diamonds correspond to experimental data obtained in an air atmosphere for \( t_{\text{UV}} = 60 \) s, and the dotted line corresponds to two-dimensional numerical simulations using \( D = 3 \times 10^{-11} \) m²/s, \( w_0 = 0.9 \) mm, \( w_j = 10 \) mm, \( \Delta w = 0.28 \) mm, and \( J_{\text{mol}}(\partial \gamma/\partial C) = 1.2 \times 10^{-11} \) N/s.

where the UV light is transmitted through the sapphire substrate before it interacts with squalane. The observed thickness modulation was only slightly reduced by about 20%. This small difference is most likely due to absorption losses in the substrate and increased reflection losses at its two surfaces.

In Figure 4, we present experimental data for the separation of the film thickness minima \( \Delta x_{\text{min}} \) as a function of time. For larger values of \( h_0 \) and shorter values of \( t_{\text{UV}} \), \( \Delta x_{\text{min}} \) tends to increase in time, whereas it decreases for thin films and longer irradiation times. The reason for the narrowing in the latter case is that Marangoni stresses are then strong enough to further contract the film thickness maximum against opposing capillary pressure gradients. For sufficiently long times, lateral diffusion removes concentration gradients and \( \Delta x_{\text{min}} \) increases as a result of capillary pressure relaxation. The solid lines correspond to numerical 2D simulations using the surface-dominated reaction model, which reproduce the experimental data quite well.

Experimental data for the dependence of the deformation amplitude on the initial film thickness are depicted in Figure 5a. Smaller values of \( h_0 \) give rise to larger values of \( \Delta h_{\text{pp}} \). Numerical data for the film thickness modulation as a function of \( h_0 \) evaluated at fixed times are plotted in Figure 5b,c on the basis of the surface- and bulk-dominated reaction models, respectively. Two different effects are at play. On the one hand, a greater film thickness translates to a higher mobility of the liquid and thus less resistance to deformation, thereby promoting an increase in modulation. Moreover, for bulk-dominated reactions, a greater film thickness implies a larger quantity of reaction products in the irradiated region. Thus, we expect that a larger value of \( h_0 \) thus tends to amplify the deformation amplitude. This expectation is confirmed in Figure 5c, where \( \Delta h_{\text{max}} \) increases monotonically with \( h_0 \). The "wiggles" are due to the coalescence phenomenon discussed in the context of Figure 2b,c, which occurs at later times for thinner films. The dotted line in Figure 5c corresponds to a power law of \( \Delta h_{\text{max}} \sim h_0^{2/3} \).
On the other hand, in the context of the surface-dominated model, the photochemical reaction occurs only in a surface layer much thinner than \( h_0 \) and the liquid underneath it serves only to dilute the reaction products. In this case, we expect a higher value of \( h_0 \) to reduce the effective concentration and contribute to a decrease in \( \Delta h_{\text{max}} \). This behavior is observed in Figure 5b for initial film thicknesses above approximately 3 \( \mu \text{m} \). For \( h_0 \lesssim 3 \mu \text{m} \), the Marangoni stresses are so strong that the film thins almost completely, i.e., \( |\Delta h_{\text{min}}| \) approaches its maximum possible value \( h_0 \). The dashed–dotted line in Figure 5b corresponds to a power law of \( \Delta h_{\text{inf}} \sim h_0^{1/2} \).

The solid lines in Figure 5a corresponding to 2D simulations according to the surface-dominated reaction model reproduce the experimental data well. We conclude that the surface-dominated model is relevant to our experimental system of squalane irradiated by a deuterium lamp. This could mean that the penetration depth of the photoactive wavelengths is much smaller than \( h_0 \) or that the reaction is governed by processes primarily occurring at the interface, after which the reaction products diffuse into the bulk.

Figure 6a–c illustrates the sensitivity of the main experimental observable \( \Delta h_{\text{max}}(t) \) with respect to variations in three key parameters: the photochemically induced rate of change of surface tension \( j_{\text{bulk}}(\partial \gamma / \partial C) \), the diffusion coefficient \( D \), and the aperture width \( w_c \). A larger surface tension increase will lead to a higher Marangoni flow and thus a higher film thickness increase. The dashed line in Figure 6a corresponds to a proportionality relation \( \Delta h_{\text{max}} \sim j_{\text{bulk}}(\partial \gamma / \partial C) \), whereas the dotted line corresponds to the power law \( \Delta h_{\text{max}} \sim \left( j_{\text{bulk}}(\partial \gamma / \partial C) \right)^{1/3} \).

A larger diffusion coefficient leads to a faster broadening of the concentration profile, which reduces the Marangoni stress and tends to decrease \( \Delta h_{\text{max}} \). The effect of \( D \) on \( \Delta h_{\text{max}} \) depicted in Figure 6b is relatively weak, especially for short times \( t \lesssim 100 \) s and small values of \( D \lesssim 5 \times 10^{-11} \text{m}^2/\text{s} \). The diffusion coefficient becomes more important for times \( t \) comparable to the diffusive time scale \( w_c^2/D \approx 2 \times 10^5 \) s.

A larger value of \( w_c \) leads to a longer coalescence time \( t_{\text{coa}} \) of the initially separate film thickness maxima (about 80 s in Figure 2b). This implies that for a fixed instance of time \( t \ll t_{\text{coa}} \), the local height profile near the perimeter of the aperture essentially corresponds to that of an infinitely wide aperture. Thus, \( \Delta h_{\text{max}} \) becomes independent of \( w_c \) in Figure 6c for sufficiently large \( w_c \). For very small values of \( w_c \), the overall quantity of photogenerated species decreases, leading to a decrease in \( \Delta h_{\text{max}} \) with decreasing \( w_c \). The dashed–dotted line in Figure 6c corresponds to the power law relation \( \Delta h_{\text{max}} \sim w_c^{1/2} \).

There is little qualitative difference between the two reaction models as far as the dependencies on \( \partial \gamma / \partial C \), \( D \), and \( w_c \) are concerned. Data analogous to that presented in Figure 6a–c but obtained with the surface-dominated model are presented as part of the Supporting Information.

A. Self-Similar Behavior. To elucidate the dominant mechanisms that govern different stages of the redistribution process, we derived self-similar solutions of the governing equations (eqs 3 and 7). A finite value of the aperture width \( w_c \) constitutes an imposed length scale, which leads to the coalescence phenomenon discussed in the context of Figure 2b and precludes self-similar behavior. Therefore, we consider here the local dynamics at the perimeter of very wide (i.e., semi-infinite) apertures. Although we can eliminate \( w_c \) from the problem in this fashion, we do have the other (imposed) length scale \( \Delta w \) to consider. Consequently, we can identify only self-similar solutions that are restricted in their validity to certain time intervals, when the solution is either no longer or not yet affected by the value of \( \Delta w \).

We assume that locally

\[
I(x, y, t \geq 0) = \Theta(-x, \Delta w) \Theta(t_{UV} - t, \Delta t)
\]

holds and first consider shallow transitions, i.e., large values of \( \Delta w \). In this case, the concentration gradients are small, and

\[
l(x, y, t \geq 0) = \Theta(-x, \Delta w) \Theta(t_{UV} - t, \Delta t)
\]
Figure 7a compares the prediction of eq 12 with full numerical solutions of $C \equiv C'(t_{UV})$ as a function of $x/\Delta w$ for $1 \times 10^{-3} \leq t \leq 4 \times 10^4$ s, i.e., more than 4 orders of magnitude in time. The curves indeed all collapse, indicating that eq 12 is an excellent approximation. Consequently, the surface tension gradient can be written in the form

$$\frac{\partial \gamma}{\partial x} = \frac{\partial \gamma}{\partial C} \approx t f(x) \text{ with } f \equiv j_{\text{bulk}} \frac{\partial \gamma}{\partial C} \frac{\partial C}{\partial x}$$ (13)

For large values of $\Delta w$, flow due to capillary pressure gradients can be neglected compared to Marangoni flow in the illuminated region. Moreover, for the initially small deformation amplitudes $\Delta h \equiv h - h_0 \ll h_0$, flow due to hydrostatic pressure gradients can also be neglected. In this case, eq 3 becomes separable and the Ansatz $\Delta h \equiv \frac{1}{2} \frac{1}{\Delta w} g(x)$ yields

$$g(x) = -\frac{h_0^2}{2\mu} \frac{\partial^2 \Theta}{\partial x^2}$$ (14)

in the limit of $\Delta h \ll h_0$. This solution is represented by the black solid line in Figure 7b, which is an excellent approximation to the full numerical solution of the full equations (eqs 3 and 7).

For a sharp transition in the reaction rate, i.e., for small values of $\Delta w$, the pressure-driven flow is locked onto the Marangoni flow because of the phenomenon of capillary choking\(^\text{17}\) (Appendix A). The Marangoni convection term scales as...
Consequently, the relation \( \tau \) far as the fluid dynamics are concerned, the exponents in the variable \( \phi(\eta) \) are scale-invariant, i.e., arbitrary positive numbers \( \alpha \). Introducing the reduced concentration \( C' \equiv C/(\Delta w)^2 \) allows us to derive (Appendix A) the following ordinary differential equation (ODE) in the self-similar coordinate \( \xi \equiv x/(D\Delta t)^{1/2} \):

\[
-\frac{\xi}{2} \frac{d C'}{d \xi} + C' = I(\xi) + \frac{d^2 C'}{d \xi^2}.
\]

The corresponding self-similar solution for \( C(\xi) \) is plotted as the solid line in Figure 7c alongside numerical solutions of the full set of equations (eqs 3 and 7) for three decades in time 0.01 \( \leq t \leq 10 \) s (symbols).

Next, we determine a similarity solution for the evolution of the height profile \( h(x, t) \). A small value of \( \Delta w \) implies that initially the Marangoni stress driving the film deformation is present only in an exceedingly narrow interval, outside of which the only driving force is given by capillary pressure gradients. Consequently, at the borders of this interval, a flux continuity condition must hold, which provides the above-mentioned linkage between capillary and Marangoni fluxes. If we set \( \tau_0 \equiv A \Delta h/(D\eta) \), where \( \eta \equiv x/(E \Delta t) \) is the self-similarity coordinate, then its validity in the region outside the narrow interval implies the capillary scaling \( x \sim \eta^2 \). Here, \( D_\beta \) and \( E \) are constants that render \( \phi \) and \( \eta \) dimensionless. The flux continuity determines the value of the exponent \( \beta = 1/4 \). For details, we refer the reader to Appendix A.

The self-similar solution for \( C \sim tC'(\xi) \) is decoupled from \( \Delta h(x, t) \) because at early times convective mass fluxes can be neglected compared to the reactive and diffusive contributions. Consequently, the effective concentration difference between illuminated and unilluminated regions scales as \( \Delta C (t \leq t_{UV}) \sim t^\alpha \) or \( \Delta C (t > t_{UV}) = \text{const} \sim t^\beta \) before and after switching off the UV light, respectively. If the width of the transition zone of the concentration distribution can be considered to be an exceedingly narrow interval despite its diffusive broadening (as far as the flow field is concerned), then the exponents in the relation \( \tau_0 \equiv A \Delta h/(D\eta) \) have values of \( \kappa_m = 1 \) and \( \kappa_d = 0 \). This implies \( \beta_m = 3/2 \) and \( \beta_d = 1/2 \), respectively. The dashed and dotted lines Figure 7b correspond to power law relations \( \Delta h \sim t^{\beta_m/2} \) and \( \Delta h \sim t^{\beta_d/2} \), respectively, which reproduce the behavior of the full numerical solutions (symbols) very well. Also, the time exponent of 1.57 in Figure 2c is close to 3/2, and the origin of the deviation is that \( \Delta w = 0.2 \) mm is not sufficiently abrupt.

We have also compared the full numerical solutions of eqs 3 and 7 for \( \Delta w = 2 \) \( \mu m \) depicted in Figure 7b with the self-similar height profiles \( \phi(\eta) \) determined from solving eq A5. The solid line in Figure 7d represents \( \phi_m \) i.e., the on stage (\( \beta = 3/2 \)), which is an excellent approximation to the numerical data (symbols) for 5 decades in time \( 10^{-4} \leq t \leq 10 \) s. The dashed line represents \( \phi_d \), i.e., the off stage (\( \beta = 1/2 \)), which approximates the amplitude and shape of the numerical data (symbols) very well for \( 40 \leq t \leq 1000 \) s. We inverted the sign of \( \phi_d \) merely to avoid excessive overlap between the curves. The apparent lateral shift between \( \phi_{\text{diff}} \) and the numerical data is caused by the progressive convection of the concentration distribution, which eq AS does not account for.

Finally, we note that in the limit of small deformations the self-similar solutions derived above are equally relevant to the surface- and bulk-dominated reaction models because the structure of eq 7 is identical in the limit of \( h \approx h_0 \).

B. Reaction Mechanism. Deep UV irradiation in an air environment can lead to ozone formation and the partial oxidation of hydrocarbon surfaces as exploited technologically for surface cleaning. Thus, our initial expectation was that ozone generation and the subsequent oxidation of squalane are likely candidates for the dominant reaction pathway. In striking contrast, the experimental results obtained in air and nitrogen atmospheres shown in Figure 3 indicate that oxygen plays more the role of an inhibitor rather than a promotor of the reaction. Consistent with our findings in Figure 3, Bruggeman et al. state that the presence of oxygen may become a rate-limiting factor because of its reactivity with short-lived hydrogen and carbon radicals.

Generally, photochemical reactions are complex and require sophisticated experimental instrumentation for the elucidation of reaction mechanisms, rates, and product distributions. Yang et al. studied the photolysis of liquid cyclohexane at 147 nm, with the primary product being cyclohexene. They concluded that the presence of benzene caused a drastic reduction in the rate of cyclohexane decomposition due to the scavenging of hydrogen atoms. Holroyd determined the principal primary process at 147 nm in n-pentane to be H₂ elimination and the formation of hydrogen atoms and pentyl radicals. Nurmukhametov et al. exposed polystyrene films and solutions to 248 nm radiation and concluded that the UV-induced reaction includes the dehydrogenation of the molecular chain and the subsequent formation of polycoujugated polyene chains. Bossa et al. developed and validated a kinetic model for methane ice photochemistry upon irradiation with UV light in the 120–200 nm wavelength range. We therefore suspect that alkene formation might not occur in our experiments. Consistent with this hypothesis, Birdi found that the surface tension values of n-alkenes are systematically higher than those of corresponding n-alkanes by approximately 0.5–1\%,1,26

One possible conclusion from Figure 5a was that squalane is an optically thick material for deep-UV radiation. Moreover, we mentioned that the measured thickness modulation is comparable for the liquid film facing up or facing down. This may suggest that the crucial requirement for the reaction is not so much the presence or absence of ambient gases but rather the presence or absence of dissolved gases in the liquid. Given the small liquid film thickness, the diffusion of gases into squalane after spin-coating requires less than 1 s, which is much shorter than the time required for mounting the sample.

C. Implications for Reaction Monitoring. The experimentally adjustable parameters of this technique are the initial film thickness \( h_0 \), the aperture size \( w_\text{ap} \), and the illumination time \( t_{\text{UV}} \). The extractable parameters are the surface tension change

\[
Q \frac{\partial C}{\partial x} = \frac{h^2}{2\mu} \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} \right)^2 \sim \frac{h^2}{2\mu} \frac{\partial}{\partial x} \left( h_\text{bulk} t^2 \right)^2.
\]

i.e., quadratically with time \( t \). Consequently, both convective terms are negligible compared to the diffusive term scaling as \( D h_\text{bulk} t/(\Delta w)^2 \), i.e., linearly with \( t \), at early times. This implies the capillary scaling –ff –ff –ff –ff. Consequently, this interval implies the capillary scaling –ff –ff –ff –ff. Consequently, both convective terms are negligible compared to the diffusive term scaling as \( D h_\text{bulk} t/(\Delta w)^2 \), i.e., linearly with \( t \), at early times. This corresponds to the limit of a large convective Damköhler number and a diffusive Damköhler number of order 1. Thus, in the limit of \( \Delta h \ll h_0 \) or equivalently \( h \approx h_0 \), the 1D reaction–convection–diffusion equation can be simplified to

\[
\frac{\partial C}{\partial t} = h_\text{bulk} I(x) + \frac{d^2 C}{d x^2}.
\]
\( \Delta \gamma = \gamma - \gamma_0 \) and the diffusion coefficient \( D \). Our experiments were restricted to a constant aperture width \( w_a = 1 \text{ mm} \), which implied that they had a low sensitivity toward variations in \( D \). According to our simulations, however, which are well validated by the gathered experimental data, we expect that smaller slit widths allow more conclusive information regarding the value of \( D \). The achievable time resolution is determined by how quickly a measurable grayscale modulation is observed in the interferometry images. On the basis of the numerical results and a required minimum thickness modulation \( \Delta h_{\text{eq}} \approx 50 \text{ nm} \), we estimate that a time resolution of several seconds is feasible for the relatively weak surface tension changes occurring in squalane. We have specifically selected squalane in order to demonstrate that relatively subtle chemical composition changes can be detected conveniently. According to eq 14, the response time will be faster for more intense irradiation, e.g., by using laser sources, for reactions that exhibit higher conversion rates or more surface-active reaction products, for thicker films, lower viscosities, and smaller values of \( \Delta \omega \).

We note further that in the dilute regime considered in this article the method is sensitive only to products \( j_{\text{bulk}}(\partial \gamma / \partial C) \) and \( j_{\text{surf}}(\partial \gamma / \partial C) \) but not independently to \( j_{\text{surf}} \) and \( \partial \gamma / \partial C \). This is a consequence of the fact that the concentration of the reaction product scales with the production rate constants \( j_{\text{bulk}} \) and \( j_{\text{surf}} \). The lubrication equation is coupled to the concentration field via the Marangoni stresses, e.g., \( \tau_z = \partial \gamma / \partial C \), which thus depend only on the above-mentioned products. Consequently, the height profile \( h \) and fluxes \( Q_z \) and \( Q_\rho \) which enter into eq 7, depend only on products \( j_{\text{bulk}}(\partial \gamma / \partial C) \) and \( j_{\text{surf}}(\partial \gamma / \partial C) \). The same, therefore, holds for the Peclet number inherent in eq 7.

V. SUMMARY

We have studied broadband deep-UV irradiation of thin liquid films of the aliphatic hydrocarbon squalane through a slit aperture. This served as a model system for monitoring photochemical reactions based on the interferometric detection of film thickness deformations. The mechanism driving material redistribution is solutocapillary Marangoni flow as a consequence of surface tension changes induced by the reaction products. Because of the differential nature of Marangoni flows, a high sensitivity of the technique can be achieved. Surface tension changes of as small as \( \Delta \gamma = 10^{-4} \text{ N/m} \) can be detected, and time resolutions below 1 s can be achieved. We performed systematic experiments where we varied the film thickness and illumination time. Interestingly, experiments performed in a nitrogen atmosphere resulted in a significantly stronger film deformation than experiments performed in either air or Ar environments. We also developed a model of the photochemical reaction and the convection and diffusion of the reaction products. Although the model takes into account only a single photoproduct species, it reproduces the experimental results almost quantitatively, if we assume that the reaction occurs primarily in a region close to the liquid surface that is much smaller than the film thickness. The main output parameter of the numerical simulations is the product of the reaction rate and the rate of change of surface tension with the photoproduct concentration. By using narrower aperture widths, information on the diffusion coefficient of the photoproduct species could also be gathered. Besides performing numerical simulations, we also derived and numerically validated self-similar solutions of the governing equations for the concentration and the height profiles, which characterize the early time response.

APPENDIX A: SELF-SIMILAR SOLUTIONS FOR ABRUPT TRANSITIONS

Introducing the dimensionless concentration \( C' = \frac{C}{h_{\text{init}}} \) implies

\[
\frac{\partial C'}{\partial t} = \frac{1}{h_{\text{bulk}} t} \frac{\partial C}{\partial t} - \frac{C}{h_{\text{bulk}}^2 t^2}
\]

or equivalently

\[
\frac{\partial C'}{\partial t} = \frac{h_{\text{bulk}} t}{C} \frac{\partial C'}{\partial t} + \frac{C}{t} = j_{\text{bulk}}(\partial \gamma / \partial C) + j_{\text{bulk}} C' \quad \text{and}
\]

\[
\frac{\partial^2 C'}{\partial x^2} = D h_{\text{bulk}} t \frac{\partial^2 C'}{\partial x^2}
\]

Equation 16 can be converted to an ODE by introducing the self-similar coordinate \( \xi \equiv x/(D t)^{1/2} \), leading to

\[
\frac{\partial C'}{\partial t} = \frac{\partial C'}{\partial \xi} = \frac{\partial C'}{\partial \xi} \left[ -\frac{D x}{2(D t)^{3/2}} \right] = \frac{\partial C'}{\partial \xi} \left[ -\frac{\xi}{2t} \right]
\]

and thus

\[
j_{\text{bulk}} \left( \frac{\xi}{2t} \right) \frac{\partial C'}{\partial \xi} + j_{\text{bulk}} C' = j_{\text{bulk}} I(\xi) + j_{\text{bulk}} \frac{\partial^2 C'}{\partial \xi^2} \frac{1}{t}
\]

\[
\Rightarrow -\frac{\xi}{2} \frac{\partial C'}{\partial \xi} + C' = I(\xi) + \frac{\partial^2 C'}{\partial \xi^2}
\]

(A1)

The lubrication equation for a narrow peak in the Marangoni stress of the form \( \tau = \lambda \delta(x) \) allows for a self-similar solution as well. Here, \( \delta(x) \) represents the Dirac delta function and \( A \) is a constant, the dimension of which depends on the value of the exponent \( \kappa \). We consider a thin liquid film of initially uniform thickness \( h_0 \) and small deformations \( \Delta h \ll h_0 \). In this case, the lubrication equation can be linearized and is given by

\[
\frac{\partial \Delta h}{\partial t} + \frac{\partial}{\partial x} \left[ h_0^2 \frac{\tau}{2\mu} + h_0^3 \frac{\gamma}{3\mu} \frac{\partial^2 \Delta h}{\partial x^2} \right] = 0
\]

(A2)

We seek a solution of the form

\[
\Delta h = D_p t^{\alpha} \phi(\eta)
\]

(A3)

where \( \eta \equiv x/(D t^{3/2}) \) and \( D_p \) and \( E \) are constants that render \( \phi \) and \( \eta \) dimensionless. Its validity in the region where the Marangoni stress is zero \(^{114-116}\) implies \( \alpha = 1/4 \). At the boundary of the narrow region, the flux must be continuous, which implies that
or $\beta = \kappa + 2\alpha$. Let us now transform eq A2 into a corresponding ODE in the self-similar coordinate $\eta$. We have

$$
\frac{\partial}{\partial t} [D_\beta \phi(\eta)] = D_\beta \phi - \alpha \frac{\partial \phi}{\partial \eta} t^{-\alpha} + D_\beta \phi \frac{\partial \eta}{\partial t} t^{-\alpha + 1} = D_\beta \phi \frac{\partial \eta}{\partial t} t^{-\alpha + 1}.
$$

(A4)

where we have used $\delta(kx) = \delta(x)/kl$. The ODE thus becomes

$$
\beta \phi - \alpha \eta \frac{\partial \phi}{\partial \eta} + \frac{d}{d\eta} \left[ \frac{h_0^2 A}{2\mu D_\beta E^2} \delta(\eta) + \frac{1}{E^2} \frac{h_0^2 A}{3\mu} \frac{\partial^3 \phi}{\partial \eta^3} \right] = 0
$$

Setting

$$
E \equiv \frac{h_0^2 A}{3\mu}
$$

and

$$
D_\beta \equiv \frac{h_0^2 A}{2\mu E^2} = \frac{A \sqrt{3h_0}}{\sqrt{\mu} \gamma}
$$

yields

$$
\beta \phi - \alpha \eta \frac{\partial \phi}{\partial \eta} + \frac{d}{d\eta} \left[ \delta(\eta) + \frac{\partial^3 \phi}{\partial \eta^3} \right] = 0
$$

(A5)

## ASSOCIATED CONTENT

### Supporting Information

Supporting Information is available free of charge via the Internet at http://pubs.acs.org/. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b00278.

Video of a typical experiment. Data supporting the negligible difference between intermittent and continuous illumination. Further simulation results analogous to Figure 6 but using the surface-dominated reaction model. (PDF)

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES


Function $\Theta(x, \Delta x)$ is zero for $x < \Delta x$ and 1 for $x > \Delta x$ and changes smoothly from zero to 1 in the interval $[-\Delta x, \Delta x]$ with continuous first and second derivatives. It is defined by a sixth-degree polynomial.


