Theoretical investigation of optical patterning of monolayers with subwavelength resolution

Triet Nguyen, Michael Mansell, Alex Small *

Physics Department, California State Polytechnic University, Pomona, CA 91768, United States

A R T I C L E   I N F O

Article history:
Received 21 December 2009
Accepted 15 April 2010
Available online xxxx
Communicated by R. Wu

Keywords:
Photolithography
Superresolution
Monolayers

A B S T R A C T

We formulate a model of monolayer patterning via optically-controlled chemical reactions, with the goal of beating the diffraction limit in photolithography. We consider the use of the proven technique of STimulated Emission Depletion (STED) to selectively place a handful of molecules in a reactive excited state. We show that repeated optical excitation has a greater effect on pattern formation than increasing the reaction rate, auguring well for experimental work. We also consider optically-controlled deposition of a soluble species via STED, and show that even for very large concentrations and excited state lifetimes the full width at half maximum of the features formed is robust against the effects of diffusion and saturation.

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1. Introduction

Due to diffraction, spatial resolution in photolithography has long been limited to approximately half the wavelength of the light used to initiate the chemical reaction in the photoreist. A variety of techniques have been proposed to overcome this limit and optically write patterns onto surfaces with subwavelength resolution, including schemes based on multi-photon absorption [1], coherent control of transitions within the photoreist molecules (via coherent population trapping) [2], and negative index materials [3]. However, achieving very high resolution in a multi-photon absorption scheme generally requires a reaction that only occurs after the simultaneous absorption of a large number of photons, making it difficult to realize resolutions significantly better than λ/4. Formation of patterns with subwavelength resolution via coherent control of transitions has only been realized in atomic vapors [4], which will not be suitable for most surface-patterning applications. Negative index materials hold the promise for potentially unlimited resolution, but are still in their early stages of development.

Here we propose to take advantage of STimulated Emission Depletion (STED), a technique that has been demonstrated to achieve λ/20 or better resolution in fluorescence microscopy [5,6]. The basic idea of STED is to first focus a pulse of light to a conventional diffraction-limited spot of size ≈ λ/2, and use it to raise the molecules to an excited state. That pulse of light is then immediately followed by a second pulse with a “doughnut” profile (i.e. a superposition of TEM_{10} and TEM_{01} modes) that has a node in the radial center of the intensity profile. The second pulse is tuned to the frequency of the downward transition, causing all of the molecules except those at the very center (where the intensity is zero) to undergo stimulated emission and return to the ground state. The result is that excitation is confined to a region with a radius at least an order of magnitude smaller than λ. When used for imaging, STED enables sub-wavelength resolution due to the fact that any photons emitted by the molecules after the second pulse must be from molecules near the node of the depletion pulse.

What we will study here is the feasibility of using the STED concept to control photochemistry, by taking advantage of the fact that excited states are often reactive. The concept was first proposed in 2004 by Hell [7], assuming a reactive ground state. We will assume a reactive excited state, since such a reaction is easier to turn “off” and thereby control. We also consider the effects of diffusion in this work. Recently, several groups have used the STED concept to achieve subwavelength resolution in photolithography, either by controlling photoinitiators [8,9] or by rendering a nonscale region of a photochromic material transparent, and using it as a mask for lithography [10]. These promising results prompt us to ask if we can approach single-molecule resolution in surface patterning via the STED concept, and produce patterned monolayers. One promising finding from our work is that (unlike in the photoinitiator approach) even a very weakly reactive species can be used to achieve subwavelength patterning of surfaces, if the exposure conditions are properly controlled.

We will consider two models of optically-controlled monolayer formation. In the first (Fig. 1), the photoreactive species is surface-bound, and excitation either causes the excited surface-
bound molecules to dissociate (with a rate constant $k$) or attach to a species in solution. An example of the dissociation scenario is rhodopsin, which undergoes a dissociation reaction in its excited state [11,12]. An example of the attachment scenario is derivatives of azobenzene, which undergoes a photocontrollable cis–trans isomerization and can be functionalized to attach to soluble species in one isomer or the other [13,14]. This model is also formally equivalent to one in which surface-bound excited species bind to a species present in solution, if the soluble species are present in excess (i.e. initial binding events do not reduce the local concentration enough to significantly reduce the rate of subsequent binding events).

However, this model is only equivalent to a system of photoreactive molecules in solution that can attach to a surface if during the excited state lifetime $\tau$ they diffuse a distance much less than $\lambda$. Since the diffusion coefficient for typical small organics in liquids at room temperature is of order $10^{-5}$ m$^2$/s [15], if STED initially confines the excited species to a region of size 10 nanometers ($10^{-8}$ m) then the excited state lifetime would have to be no larger than $10^{-7}$ seconds for this model to be applicable. The second model then explores the effect of a long-lived excited state in a diffusible and photoreactive species. In this model, we assume that a population of excited molecules is created in solution with a Gaussian profile, and model the attachment of excited molecules to the surface. We will show that getting a significant number of molecules to attach to a surface in a single activation cycle is a challenge for realistic reaction rates and concentrations, but that the width of the surface concentration profile is robust against the effects diffusion and saturation.

2. Photoactivation of surface-bound species

2.1. Model

In modeling surface-bound photoactivated molecules, we will assume (for simplicity) that surface-bound molecules are initially present on a surface with some concentration $c_i(r)$ (which will typically start out uniform). For convenience, we will write the concentration as $c(r) \equiv c_{\text{surf}}(r)$ where $c_{\text{surf}}$ is the density of sites available on the surface and $\phi$ is the fraction of sites occupied. We will calculate the fraction of sites occupied by molecules in the ground and excited states, denoted $\phi_g$ and $\phi_e$. We assume that the molecules are first raised to the excited state by a pulsed excitation beam tuned to the absorption maximum of the ground state, and we approximate its intensity profile at the surface as a Gaussian of the form:

$$I_e(r) = I_1 e^{-|r|^2/2}$$

where $r$ is the radial distance from the origin, $I_1$ is the intensity (units of photons per area per time) at the center of the beam, and $k_1$ is the wavenumber (in the surrounding medium) of the excitation beam.

We will assume that our molecules have 3 energy levels, as shown in Fig. 2. The reactive state is assumed to be $|2\rangle$. In reality, the two excited states shown will be part of a larger set of singlet excited states coupled by vibrational transitions, but the scheme in Fig. 2 suffices for our purposes. We assume optical excitation from the ground state $|1\rangle$ to the highest state $|3\rangle$, and that the rate of spontaneous radiative transitions from $|3\rangle$ to $|1\rangle$ is negligible compared to the rate $\tau_e^{-1}$ for vibrational transitions from $|3\rangle$ to $|2\rangle$. For organic fluorophores, $\tau_e$ is often of order $10^{-11}$ to $10^{-13}$ seconds, while the radiative lifetime of the excited state is typically of order nanoseconds or longer [16].

In the steady state, the kinetic equations describing the populations of these states are:

$$\frac{d}{dt}N_1 = \sigma_e I_e(N_3 - N_1) + N_2/\tau = 0$$

$$\frac{d}{dt}N_2 = N_3/\tau_e - N_2/\tau = 0$$

$$\frac{d}{dt}N_3 = \sigma_e I_e(N_1 - N_3) - N_3/\tau_e = 0$$

where $N_1$, $N_2$, and $N_3$ are the fraction of molecules in the 3 energy levels.

We assume that the pulse duration is shorter than the time scale for reactions, so the fraction of sites occupied by excited molecules (in state $|2\rangle$) immediately after the excitation pulse can be found from solutions to the kinetic equations (3)–(5):

$$\phi_e(r) = \phi_{g,i} \frac{\sigma_e \tau I_e(r)}{1 + \sigma_e I_e(r)(\tau + 2\tau_e)}$$

$$\approx \phi_{g,i} \frac{I_e(r)}{1 + I_e(r)(1 + 2\tau_e/\tau)}$$

where $\phi_{g,i}$ is the fraction of sites occupied by molecules in the ground state before excitation, $\sigma_e$ is the absorption cross section of the ground state at the frequency of the excitation beam, and $\tau$ is the radiative lifetime of the excited state. We are assuming that the time intervals between excitation events are long compared to the excited state lifetime. The last term in the denominator will hereafter be neglected, because the lifetime of vibrational transitions is generally at least an order of magnitude smaller than the lifetime of radiative transitions.
The subsequent depletion pulse that returns molecules to the ground state via stimulated emission is approximated with a spatial profile of the form:

\[ I_d(r) = I_2 k_2^2 e^{-r^2 k_2^2/2} \]  

(7)

where \( I_2 \) also has units of photons per area per time and \( k_2 \) is again the wavenumber (in the surrounding medium) of the depletion pulse. If the pulse duration \( \Delta t \) (as well as the time elapsed between the end of the excitation pulse and the beginning of the second pulse) is significantly shorter than the lifetime of the excited state, then the concentration of molecules in the excited state after the STED beam is:

\[
\phi_e(r) = \frac{I'_e(r)}{1 + I'_e(r)} e^{-\sigma_1 I_d(r) \Delta t} \\
= \frac{I'_g(r)}{1 + I'_e(r)} e^{-\sigma_1 t_d}
\]

(8)

where \( \sigma_1 \) is the stimulated emission cross-section of the excited state, \( I'_e(r) = \sigma_1 \tau \sigma_2 \), and \( I'_g \) is the initial condition for \( \phi_e \).

For large \( I_d \), after the sequence of pulses the excitation is confined to a region close to the origin, where \( I_d \approx 0 \) because of its \( r^2 \) dependence. If \( I_d \) is small then \( \phi_e(r) \) is a bell-shaped curve with the usual width for STED microscopy, \( \approx \sqrt{\lambda} \sqrt{1 + I_2 \sigma_1 \tau} \) (assuming that the wavelengths of the two pulses are similar, as is usually the case). If, however, \( I'_e \approx 0.1 \) or greater (i.e. the rate of excitation begins to approach the same order of magnitude as the rate of spontaneous emission), a necessary condition for bringing a large fraction of the surface-bound molecules into the reactive excited state in each cycle then \( I'_e/(1 + I'_e) \) begins to saturate and the resolution changes. We can work out the relationship between resolution and excitation intensity by expanding Eq. (8) near the origin to second order in \( r \). The result is:

\[
\frac{\phi_e(r)/\phi_{e,i}}{1 + I'_e(r)} \approx \frac{l'_1}{2} \left(1 - \frac{r^2 k_1^2}{2} \right)
\]

(9)

where \( l'_1 = l_1 \sigma_1 \tau \) and \( l'_2 = l_2 \sigma_1 \Delta t \). The first two terms in the numerator of the coefficient of \( r^2 \) are familiar from traditional STED microscopy. The \( l'_1 \) in the denominator and the other numerator term, however, occur because at high excitation intensity the upward transition intensity is approximated with a spatial width for STED microscopy, \( \approx \lambda/\sqrt{1 + I'_2} \). The first term in the denominator would only matter in a situation where \( l'_1 \) is small and \( l'_2 \) is large. In that case, due to the high excitation intensity even those molecules much more than \( \lambda \) away from the center would be raised to the excited state by the intense tail of the excitation beam, and very few of them would return to the ground state, reducing the resolution of the patterning approach.

The subsequent depletion pulse that returns molecules to the ground state via stimulated emission is approximated with a spatial profile of the form:

In what follows, we use the spatial profile given in Eq. (8) as the initial condition for \( \phi_e(r, t) \) and \( \phi_{e, i} - \phi_e(r, t = 0) \) as the initial condition for \( \phi_{e, i} \). These concentration profiles obey the following equations:

\[
\frac{d}{dt} \phi_e = -\phi_e/\tau - k_d \phi_e - k_b \phi_e \\
\frac{d}{dt} \phi_{e,i} = \phi_e/\tau
\]

(11)

(12)

where \( k_d \) is the (first order) rate constant for dissociation from the surface, \( k_b \) is the rate at which excited molecules photobleach, and \( \phi_e/\tau \) is the spontaneous emission rate. Solving these coupled linear equations gives the following result for the number of molecules in the ground state and attached to the surface at \( t > \tau \) (i.e. after all of the molecules still attached have returned to the ground state):

\[
\phi_g(r) = \frac{I'_g(r)}{1 + I'_e(r)} e^{-\sigma_1 I_d(r) \Delta t} \left( k_d + k_b \right) \frac{\tau}{1 + (k_d + k_b) \tau}
\]

(13)

Since bleaching and dissociation rates always enter this model additively, there is no need to vary these parameters separately to understand the behavior of the model. From a practical standpoint, however, it is desirable to have \( k_d \gg k_b \). For the remainder of this work, we will only treat the case \( k_d = 0 \). If \( k_d \neq 0 \), the ratio of dissociated to bleached molecules can be calculated from the ratio \( k_d/k_b \).

2.2. Key results for photodissociation of surface-bound molecules

Eq. (13) can be used to calculate the number of molecules attached to the surface after illumination by excitation and depletion pulses of arbitrary beam profile, not just the profiles in Eq. (1) and Eq. (7). For illumination by a series of alternating excitation and depletion pulses, \( \phi_{e,i} \) is whatever the local concentration was after the previous exposure. We assumed simultaneous illumination by several pulses of the forms in Eq. (1) and Eq. (7), centered at different locations and (possibly) having different intensities. We calculated the local concentration after the exposures, and then repeated the calculations for a new set of beams. All calculations were performed in Matlab.

For validation of the code, we also implemented a discrete model, where arrays of molecules with \( \lambda/500 \) spacing were simulated. A molecule’s probability of dissociating from the surface is equal to the right-hand side of Eq. (13) and is assumed to be unaffected by the status of its neighbors. At the end of each simulation, a site was either occupied or unoccupied. By running many simulations, counting the number of times that a molecule dissociated from a site, and dividing by the number of simulations run, we obtained average concentration profiles. Many stochastic simulations were performed and averaged, and the results were compared with calculations from the concentration model of Eq. (13) to validate the code. Because the stochastic simulations and the direct calculations from Eq. (13) both use the same probability model, it is not surprising that they gave the same results. We only used the stochastic simulations as a check on our code. All results reported here will be based on direct calculations from Eq. (13).

We will assume that the excitation beam has a wavelength of 500 nanometers, and that the depletion beam has a wavelength of 525 nanometers, representing common peaks in the absorption and emission spectra of organic dyes in the visible region.

Our key finding comes when we compare the effects of increasing the number of exposures and increasing the rate constant. Eq. (13) is messy to manipulate analytically, but it is clear that

**Please cite this article in press as:** T. Nguyen et al., Physics Letters A (2010), doi:10.1016/j.physleta.2010.04.038
raising it to a positive integer exponent (due to multiple exposures with the same beam profile) can give an arbitrarily small value of $\phi_0$, while increasing $k_d$ arbitrarily cannot make $\phi_0$ any smaller than $1 - \frac{1}{e} \exp(-\sigma_1 d(t) \Delta t)$. Moreover, the incremental reduction in concentration due to multiplying $k_d$ by a scaling factor $s$ is exponential in $s$, but the effect of going from 1 exposure to $s$ exposures is exponential in $s$. Note that we assume that all exposures are done by a lens focused on the same site for the duration of several consecutive pulses, without moving. Jittering can, of course, be an issue in scanning microscopes, and thus limit the resolution, but the situation we envision at least minimizes these issues somewhat because there is no motion of the lens between exposures.

To get a sense of typical values, in Fig. 3 we consider the case $I_1 = 1$ (strong excitation) and $I_2 = 8$, for different numbers of exposures and values of $k_d \tau$. In all three cases shown, the concentration profile has a dip with a full width at half maximum (FWHM) of $\approx 50 \text{ nm} \left(\lambda/10\right)$. If we first work with a weakly photoreactive species ($k_d \tau = 0.1$, i.e. reaction rate much slower than the decay of the excited state) only about 5% of the molecules are removed in a single cycle. Increasing $k_d \tau$ to 1 (factor of 10 increase) results in the removal of 25% of the surface-bound molecules in a single step. On the other hand, if $k_d \tau = 0.1$ but the exposure process is repeated 10 times, 38% of the molecules are removed. Even larger disparities in favor of repeated exposure are found as the number of exposure cycles is increased. Because multiple exposures are likely to be almost trivial to implement, while the design of a more photoreactive species is likely to be a highly non-trivial task in synthetic chemistry, this fractionalization effect is encouraging.

Additionally, we considered the effects of exposing two nearby regions simultaneously with beams centered at two different points (Fig. 4). One might consider a scheme in which parallelism is achieved by sending light through a diffraction grating to produce multiple spots, which are then focused simultaneously. As in Fig. 3, we used the parameters $I_1 = 1$, $I_2 = 8$, and $k_d \tau = 1$. For beam separations of $d = 500 \text{ nm}$ (i.e. the excitation wavelength) the concentration profile has two distinct dips (top of Fig. 4), with 25% of the molecules removed at each spot. As the beam separation $d$ decreases, the concentration dip (i.e. amount of molecules removed) does not change significantly until approximately $d = 0.6\lambda$, where 21% of the molecules are removed (middle of Fig. 4). Interestingly, however, the region in which significant numbers of molecules are removed is slightly narrower. As the separation continues to decrease, when $d = \lambda/2$ (bottom of Fig. 4) the concentration dip is only half of its original value (12% of the molecules removed instead of 25%). Taken together, these results show that while the use of STED can enable optical monolayer patterning with feature sizes much smaller than the wavelength of light, the smallest possible distance between two features being printed simultaneously is approximately $0.6\lambda$, comparable to the conventional diffraction limit. Thus, diffraction does not limit feature size, but it does limit the degree of parallelism possible in this scheme, by limiting the achievable distance between spots.

3. Diffusion of photoactivated species

3.1. Model and parameters

The model described above is applicable to photoactivated molecules attaching to a surface from solution as long as the lifetime is sufficiently short that the molecules do not have enough time to diffuse outside of the initial activation region before returning to the ground state. Here we explore the effects of diffusion when the lifetime is long, to estimate how robust resolution is against changes in wavelength, initial concentration in solution, or surface reactivity.

We will assume that excited (and hence reactive) molecules are initially present in solution at a concentration $C_s(r)$. The effect of the excitation and depletion beams is to confine the excited molecules to a region with a Gaussian profile centered at the coordinates $(r, z) = (0, 0)$ (see Fig. 5). We approximate the initial concentration profile $C_s$ (the subscript $s$ stands for “solution”) of excited molecules with:

$$C_s(r, t = 0) = C_0 e^{-\left((r^2 + z^2)/4\right)}/R^2$$

where $R$ is the (lateral) width ($1/e^2$ measure) of the Gaussian and the $1/4$ coefficient on $z^2$ reflects the fact that focused laser beams tend to be better localized along the lateral direction than the axial direction.

We will denote the concentration of molecules attached to the surface as $c \equiv C_{sat} \phi$ as above. We will assume that initially the surface has no molecules attached, so $\phi(r) = 0$ at $t = 0$. In solution, the time dependence of the concentration profile of excited
molecules is governed by diffusion and decay from the ground state, giving the following equation:

$$\frac{\partial}{\partial t} C_s = D \nabla^2 C_s - C_s / \tau$$ (15)

At the surface, the concentration of attached molecules is governed by second order kinetics, with a maximum surface concentration, giving the following time dependence:

$$\frac{\partial}{\partial t} \phi = k_{\text{on}} C_s (1 - \phi) - k_{\text{off}} \phi$$ (16)

where $1 - \phi$ is the fraction of sites unoccupied.

These equations for the time evolution of $\phi$ and $C_s$ must be supplemented by boundary conditions. We assume that this reaction happens in a large cylindrical container, and we impose no-flux conditions at the radial edge and at the top surface ($r = 10R$ and $z = 10R$ in our simulations). At the reaction surface ($z = 0$) we impose the condition that the flux of molecules from solution onto the surface (given by Fick’s Law) be equal to the rate at which molecules accumulate on the surface:

$$D \frac{\partial}{\partial z} C_s = \frac{\partial}{\partial t} C_s = k_{\text{on}} C_s (1 - \phi) - c_{\text{sat}} k_{\text{off}} \phi$$ (17)

We will assume that the molecules are tightly bound to the surface (i.e. binding energy $\gg k_B T$) so that $k_{\text{off}} \approx 0$ and the off rate will be ignored hereafter. To non-dimensionalize the equations, we will measure distances in units of the Gaussian concentration width of the surface profile is hence equal to the width of the initial concentration profile in solution, and so nanoscale resolution on the surface is easy to obtain if the initial concentration profile in solution has a narrow width due to the use of stimulated emission depletion. However, if either condition is violated, so that $\tau' \equiv k_{\text{on}} / D k_{\text{off}}$. The boundary condition on $C_s$ at $z' = 0$ is given by:

$$\frac{\partial}{\partial z'} C_s = k' C_s (1 - \phi)$$ (20)

Our dimensionless quantities are summarized in Table 1.

3.2. Results from model

As a first step, our model is easy to solve in the limit where $\tau' \ll 1$, the excited state decays before molecules can diffuse a distance comparable to the $1/e^2$ width $R$ of the initial concentration profile, and the time dependence of the concentration in solution is just an exponential decay. If the total amount of molecules deposited is also small, then the $(1 - \phi)$ term in Eq. (18) and Eq. (19) does not change significantly during the lifetime of the excited state, and so the final surface concentration is:

$$\phi(r) = \int_0^{\infty} C_s(t = 0) e^{-t'/\tau'} dt' = C_s(t = 0) k' \tau'$$ (21)

In this case, the concentration profile on the surface is directly proportional to the local concentration profile in solution. The $1/e^2$ width of the surface profile is hence equal to the width of the initial concentration profile in solution, and so nanoscale resolution on the surface is easy to obtain if the initial concentration profile in solution has a narrow width due to the use of stimulated emission depletion. However, if either condition is violated, so that $\tau' \geq 1$ and/or $\phi \approx 0.1 - 1$ after the excited state has decayed, then the width of the surface concentration profile may be greater than the width in solution, reducing the resolution. In the case of long-lived species, the reduction in resolution comes from diffusion of the soluble species, increasing the width of the concentration profile in solution over time. In the case of large surface concentrations, saturation effects will cause the deposition rate to drop near the center of the profile while remaining steady near the edges, broadening the profile.

To determine the magnitude of these effects, we conducted simulations of a “worst case scenario”: We first determined the necessary volume concentration (i.e. value of $C_s^\prime$) so that the peak concentration on the surface is $\phi = 0.5$, for a range of different lifetimes $\tau'$ and reaction rates $k'$. We then determine the surface concentration profile’s full width at half maximum (FWHM) under those conditions. Simulations were performed in COMSOL Multiphysics, using the Chemical Engineering module in axisymmetric mode. The boundaries of the computational window were given by $0 \leq r', z' \leq 10$ (see Fig. 5). The mesh comprised 18,021 elements, with a higher density near the $z' = 0$ surface where the reaction occurs.

![Fig. 5. Initial condition for binding of a diffusible, photoreactive molecule to a surface. The initial concentration profile is a Gaussian centered at $t = R = 0$. The reactive surface is at $z = 0$ and the boundaries of the window are at $10R \times 10R$ Gauss'ian's $1/e^2$ width $R$. The system is axisymmetric about the $z$-axis.](image-url)
As shown in Fig. 6, the concentration required to achieve a maximum of 50% surface coverage decreases (not surprisingly) as the reaction rate increases. For long lifetimes (relative to the characteristic diffusion timescale $R^2/D$) the required concentration is largely independent of the excited state lifetime, as after a time of order $R^2/D$ most of the excited molecules have diffused away from the surface. The most important point is that if the reaction rate constant $k'$ is small ($< 1$), so that the characteristic reaction time is longer than the characteristic diffusion time, highly concentrated solutions $C_0' > 10^2$ are required. Since a value of $C_0' = 1$ corresponds to approximately $3 \times 10^{-2}$ M, values of $C_0'$ larger than 100 are unrealistic in most cases. This does not rule out the feasibility of working with weakly reactive species, as the logic of using multiple cycles (as above) still applies. Interestingly, due to the effect of surface binding on the concentration profile in solution and the non-linearity of Eq. (18) and Eq. (19), the required concentration is not directly proportional to the inverse of the rate constant $k'$, although it does decrease as $k'$ increases.

With those required concentrations established for different excited state lifetimes and reaction rate constants, we next examine the FWHM of the surface concentration profiles. (We used FWHM rather than 1/$e^2$ with simulation data because it is easy to infer from a visual examination of a graph.) As shown in Fig. 7, the FWHM of the surface concentration profile (normalized to $R$, the 1/$e^2$ width of the initial Gaussian profile of molecules in solution) is quite robust against large changes in excited state lifetime and reactivity. In the ideal case, where the profile on the surface matches the initial Gaussian profile in solution, the FWHM would be $\sqrt{\log 2} R = 0.833 R$ (from the condition $e^{-r^2/R^2} = 0.5$). For short excited state lifetimes (less than the characteristic diffusion time) the FWHM is close to this value (within 25%), because most of the attachment to the surface happens before the profile of the excited molecules in solution can be broadened by diffusion. Even for excited state lifetimes two orders of magnitude longer than the diffusion time scale, however, the width FWHM is only about twice the ideal value. The key reason for this is that at long times most of the excited molecules have diffused away from the surface. Therefore we conclude that while diffusion effects may pose problems for attaching large numbers of molecules to the surface, they will not significantly broaden the surface concentration profile.

4. Conclusions

In conclusion, we have formulated theoretical models of optical-ly-controlled patterning of monolayers via STimulated Emission Depletion in two different scenarios: Excitation of a surface-bound species for either selective removal or attachment to a soluble species, and excitation of a soluble species that attaches to a surface while in its excited state. Achieving significant attachment of a soluble species during its excited state lifetime is likely to require either very fast reaction rates or very high concentrations, due to the diffusion timescale being so short ($\approx 10^{-7}$ seconds). However, diffusion effects do not significantly impair resolution, and repeated cycles of exposure and reaction can be used to accumulate molecules on a surface with very high spatial resolution.

Moreover, reactions involving an excited species that is already bound to the surface can also lead to surface patterning with very high resolution, but this concept faces no constraints due to diffusion. One promising way of realizing this concept is with a reaction in which an excited surface-bound species (e.g. a metastable structural isomer) binds a diffusible molecule while in its excited state; due to the potentially long lifetimes of such molecules, significant attachment could be realized in a single cycle of activation and reaction. An additional benefit of working with surface-bound excited species is that repeated exposure has an exponential effect on the number of unreacted molecules remaining on the surface, while increasing the rate constant has only a linear effect. Because increasing the number of exposures is almost trivial (requiring multiple laser pulses, provided that the point of focus is stable throughout the process) and does not require the trial and error of synthesizing a photoreactive molecule with a larger rate constant, there is great promise for patterning surface-bound molecules via STED.

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