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Role of Surface Adsorption in the Surface-Enhanced Raman Scattering and Electrochemical Detection of Neurotransmitters

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Abstract

The strength of the analyte-substrate interaction is a key component when evaluating the observed enhancements in surface-enhanced Raman scattering (SERS) detection. By performing Raman and electrochemical measurements on a series of neurotransmitters, including dopamine, serotonin, norepinephrine, and epinephrine, as well as catechol as it allows us to examine the diol moiety without the side chains present, we were able to correlate surface chemistry with the measured SERS signal and examine the oxidation mechanism of each analyte. Finite element simulations of fluid flow, mass transport, and Langmuir adsorption to a surface in a microchannel were used to expand on the experiments. By holding k_{ads} constant and changing k_{des} , K_{eq} was varied systematically to elucidate how the adsorption kinetics change for different molecular adsorbates. The modeling indicates that the largest surface concentration is observed from the analyte with the strongest affinity for the surface in both the continuous flow and time dependent injection scenarios. The COMSOL model of varying surface concentration explains differences observed in integrated current during amperometry and signal intensities in SERS measurements. This combination of results indicates that molecular structure and surface affinity influence the sensitivity in SERS, such that the species with the strongest affinity for the surface has the highest signal-to-noise in the SERS experiments in flowing solutions.

Introduction

An increased understanding of the mechanism that gives rise to a signal enhancement when an analyte is adsorbed onto a noble metal nanostructure has made surface-enhanced Raman scattering (SERS) a powerful tool for sensitive chemical detection.¹⁻² However in the condensed phase, the affinity of the analyte to the enhancing nanostructures is a key component that is often overlooked in SERS detection.³ If there is little or no affinity, then no signal will be observed because the enhancement is selective for molecules near the metal surface. The strength of the interaction can range from a weak physisorption to a strong chemisorption, but some type of sorption is necessary for obtaining a measureable SERS signal.⁴⁻⁶

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Many studies have used SERS to probe adsorption properties at metal surfaces by attaching reporter molecules with strong covalent bonds to noble metals.^{1, 7-9} Examining the SERS signal of these systems with respect to pH changes^{3, 10-12}, electrochemical potential^{10, 13}, and temperature³ allows for the elucidation of the analyte-substrate interaction. Molecules adsorbed at surfaces have been used to evaluate the distance dependence of the SERS effect.¹⁴⁻¹⁶ While gaining valuable information, these surface bound species are at fixed distances from the substrate, ignoring the situation where molecules are free to diffuse away from the substrate. In this case the affinity between the analyte and the substrate is crucial. Recently, the signal intensity fluctuations of particles in solution observed using SERS correlation spectroscopy suggested that there is impeded diffusion at the surface such that signal arises only from particles that show a favorable interaction.⁶ Other work supports this as molecular adsorption was shown to increase the SERS limit of detection for analytes in flowing solution.¹⁷ The conclusion being the role surface chemistry plays in the SERS signal is important for characterizing an analyte of interest.

Many electrochemical studies have investigated the adsorption dynamics of neurotransmitters, due to their importance in biological systems.¹⁸⁻²¹ Fast-scan cyclic voltammetry (FSCV) using carbon-fiber microelectrodes has been the primary technique to detect these biogenic amines with great sensitivity and selectivity,²⁰⁻²¹ as well as probe catecholamine adsorption and desorption.¹⁸ This technique was further improved by utilizing the adsorption properties of those species to measure absolute concentrations without employing flow to alter the concentration.¹⁹ Known as fast-scan controlled-adsorption voltammetry, the approach was able to show the distinct adsorption properties of these analytes that influence the strength of adsorption and the sensitivity on a carbon-fiber microelectrode. While carbon-fiber electrodes are mainly used because of their biocompatibility, gold electrodes have also been employed for biological applications due to the surface modifications that can be done to improve detection.²²⁻²³ Gold microelectrodes were shown to have a larger saturation coverage, as well as a higher linear range than carbon fiber, but a smaller potential window hinders its usefulness.²⁴

In this study, we examine what role these distinct adsorption dynamics play in the SERS response *in situ* by utilizing a sheath-flow microfluidic device that allows for both electrochemical and SERS measurements to be taken in a dynamic, flowing system.²⁵ The fast moving sheath-flow confines the analyte within a region above the surface and promotes analyte-substrate interactions. The fluid dynamics enable the control of the flux to the SERS electrode, improving both electrochemical and SERS sensitivity when compared to other detection methods. The combination of Raman and electrochemical experiments with finite element analysis is used to correlate surface chemistry with SERS signal. The results indicate that the molecular structure and adsorption coefficient of each neurotransmitter influences the binding affinity, and in-turn the SERS efficiency.

Experimental

Materials and Reagents

Dopamine hydrochloride, norepinephrine (98%), catechol (99%), epinephrine, serotonin, sodium phosphate monobasic dihydrate (>99%), and sodium hydroxide (NaOH, 99.99%)

were purchased from Sigma-Aldrich. Sodium phosphate dibasic was purchased from Electron Microscopy Sciences. Phosphate buffer was made using sodium phosphate monobasic dihydrate and sodium phosphate dibasic. The pH was adjusted by adding NaOH while monitoring with an Accumet Basic AB15+ pH Meter. Ultrapure water (18.2 M Ω cm) was obtained from a Barnstead Nanopure filtration system. Polydimethylsiloxane (PDMS) devices were made using Sylgard 184 elastomer base (Ellsworth Adhesives, Germantown, WI, USA) from masters fabricated with SU-8 50 photoresist and Nano SU-8 developer (Microchem, Newton, MA, USA). Polystyrene bases were made with polystyrene powder (250 μ m particle size, Goodfellow, Huntingdon, England), fused silica capillary (360 μ m o.d., 150 μ m i.d., Molex), and a gold wire electrode (25 μ m diameter, Alfa Aesar, Ward Hill, MA, USA). The electrode was connected to a copper wire with colloidal silver (Ted Pella, Redding, CA, USA). A commercial gold plating solution (OROTEMP® 24 RTU RACK, Technic Inc.) was used for all electrodeposition. All other chemicals were analytical grade and used without any further purification.

SERS Flow Cell Device

The fabrication of the polystyrene-encapsulated electrode and fluidic tubing was performed as previously reported.²⁶ A 25 μ m gold (Au) electrode was embedded approximately 110 μ m away from the center of a 150 μ m i.d. capillary. The encapsulated Au electrode was made SERS-active by electrodepositing Au onto the surface. A PDMS reservoir was positioned around the electrode and the Au plating solution placed inside. Au was deposited at a potential of -1.2 V vs. Ag/AgCl, applied for 200 seconds, to form the SERS active surface. The Raman signal of the deposited Au SERS electrode was improved by running an oxidation-reduction cycle, with flow, to electrochemically roughen the surface and remove any contaminants as previously reported.²⁵ The same Au SERS electrode was used for consecutive SERS detection experiments.

In situ measurements were performed using a 250 μ m wide by 100 μ m high channel molded in a thin film of PDMS. A 20:1 mixture of the elastomer base was poured onto a silicon master and heated at 65°C for 1 hour. The PDMS chip was cut to form an inlet hole and a reservoir for solution collection and positioned over the SERS-active electrode in line with the capillary and SERS-active electrode. Solution is driven via a syringe pump (Model NE-1000, New Era Pump Systems Inc., Farmingdale, NY) through both the inlet-hole in the PDMS channel and the embedded capillary. Hydrodynamic focusing of the capillary solution is achieved by pumping the sheath flow continuously through the inlet. The sheath flow was 5 μ L/min and the capillary flow was 1 μ L/min for all experiments. The ratio of the sheath and capillary flow rates optimizes the focusing effect, as previously reported.²⁵

Raman Measurements

Raman spectroscopy was performed using a 17 mW (cw), 632.8 nm HeNe laser. The laser output was filtered through a laser line filter (Semrock), a broad band polarizer (ThorLabs) and half-wave plate (ThorLabs) to control the polarization and attenuate the power. The excitation beam was then reflected off a 45° 633 nm dichroic mirror and directed into the objective lens. The sample was illuminated through a 40 $\times$ water immersion objective (Olympus, NA=0.8) and the power measured at the sample was 1 mW. Raman back

scattering was collected through the same objective and transmitted to the spectrograph (Shamrock 303i, Andor) with a 600 gr/mm grating and EMCCD (Newton 970, Andor). Spectra were recorded in kinetic series with 500 or 100 ms acquisition times.

Electrochemical Measurements

Electrochemical measurements were made using a CH Instruments Model 660D Potentiostat. The embedded SERS electrode functions as the working electrode with a platinum wire auxiliary and Ag/AgCl reference electrode placed at the end of the microchannel in the waste reservoir. All potentials in this manuscript are referenced versus Ag/AgCl and 0.1 M phosphate buffer is the supporting electrolyte. Amperometric detection was performed using a Valco 4-port injector with an internal 100 nL sample loop (Vici) to inject the neurotransmitter of interest. The microelectrode was held at a constant potential of 0.9 V for all amperometry measurements. Cyclic voltammetry for all the neurotransmitters were done on the deposited Au electrode. The scan rate was 1.0 V/s and the potential was swept from -0.5 to 0.8 V. The concentration of all analytes (in a 0.1 M phosphate buffer supporting electrolyte) was 1 mM. All solutions were degassed by bubbling Argon through them for 20 minutes.

COMSOL Simulations

Commercial finite element analysis software, COMSOL Multiphysics 4.4a (COMSOL Inc., Burlington, MA), was used to model the adsorption and desorption kinetics at a surface in a microchannel. The system simultaneously describes fluid flow, mass transport, and adsorption of analytes to a microsurface. A 2-D representation of the flow channel was designed in the CAD setting of the program that consisted of a rectangular channel intersecting with a rectangular channel with dimensions matching the capillary (150 μm i.d.) and microchannel (250 μm wide and 100 μm high). A 25 μm surface was placed 100 μm away from the capillary.

Laminar flow was modeled using Navier-Stokes equations at the steady-state. The time-dependent mass transport of the solute molecules inside the capillary and channel was modeled using Fick's law as follows:

$$\frac{\partial c_a}{\partial t} + \nabla \cdot (-D_a \nabla c_a) + u \cdot \nabla c_a = 0$$

where D_a is the diffusion coefficient (m^2/s), c_a is the analyte concentration (mol/m^3), and u is the velocity vector (m/s).

The sample analyte, A, has a concentration of 1 mM and enters the channel through the capillary where it can adsorb or desorb from sites on the surface, S, according to:

where the rate of adsorption and desorption depends on the concentration of analyte in the fluid flow, A , and the concentration of surface adsorbed species, AS .

$$r_{\text{ads}} = k_{\text{ads}} c_A \quad r_{\text{des}} = k_{\text{des}} c_{\text{AS}}$$

The variables k_{ads} and k_{des} are rate constants that govern adsorption and desorption from the surface. The reaction rate for surface species A becomes:

$$\frac{d_{c_{s,A}}}{dt} = r_{\text{ads}} - r_{\text{des}}$$

By altering the rate coefficients we can simulate how analytes with different surface affinities will interact with the surface. Table 1 shows the parameters used for each model analyte.

The model was used to simulate two different scenarios. The first is continuous flow where 1 mM of analyte is continually injected into the sample capillary from $t=0$, until a steady-state is reached. The system was also modified to examine an analyte pulse of a certain volume being introduced and transported through the microchannel. In this scenario the sample pulse is described by a Gaussian distribution with a peak concentration of 1 mM.

Results

On-Chip SERS Detection

Raman measurements were completed on a series of analytes including serotonin (5-hydroxytryptamine, HT), dopamine (DA), epinephrine (EP), norepinephrine (NE), and catechol (CAT). Figure 1 shows the oxidized and reduced structure for each molecule. Each analyte was pumped at a concentration of 2.0 mM from the sample capillary and focused onto the same SERS electrode, at open circuit potential, by the faster moving sheath flow. Figure 2a shows the average SERS spectrum over a 2 second period of each neurotransmitter. The spectra have vibrational bands matching previous SERS studies on gold and silver surfaces.²⁷⁻³² The intense bands relate to the phenol moiety, in particular the ring mode to which the hydroxyl groups are attached. This suggests that the phenol moiety adsorbs onto the surface.

The signal-to-noise (S/N) ratio of the most intense band in the SERS spectrum of HT, DA, EP, NE, and CAT is shown in Figure 2b. Under the same conditions, HT has the largest S/N ratio, while CAT has the lowest. The differences in the neurotransmitters structure could play an important role in these differences. HT has an indole functional group with a primary amine that is known to be attracted to the SERS surface.³³⁻³⁴ DA, EP, and NE all have the catechol functional group with the main structural difference being the additional alkyl-amine substitution on the benzene ring. CAT lacks this additional substituent.

SERS detection of transient concentration was measured by injecting 100 nL of each neurotransmitter into the capillary at open circuit potential. The previous experiments examined the role of adsorption with continuous flow; to expand on those results the signal in the injection experiment was monitored continuously with a 100 ms acquisition time. Figure 3a shows the SERS intensity profile of the largest band for each analyte (Figure 3b). The time for each molecule to elute from the capillary is approximately the same, with minor changes being attributed to the slight differences to the point of injection. HT has the largest peak width in the SERS injection, suggesting it has a stronger binding affinity for the gold surface than the other neurotransmitters. While DA also has a larger peak width, NE, EP, and CAT are all much sharper and show fluctuating signals.

On-Chip Amperometric Detection

Amperometric measurements were performed by monitoring the oxidation of each neurotransmitter while holding the SERS electrode at a constant potential of 0.9 V. Figure 4a shows the current versus time curves for consecutive injections of each analyte. EP, DA, NE, and CAT demonstrate consistent signal for subsequent measurements, while HT has a lower current each successive injection. HT has been shown to foul gold electrode surfaces over time, limiting the response, which would explain the decrease in signal.³⁵⁻³⁶ However, the fouling of the surface is suggestive of improved adsorption, which may explain the larger SERS response.

The relative number of each neurotransmitter interacting at the SERS electrode was determined by amperometry. Figure 4b compares the peak area of each analyte from injections of equivalent numbers of molecules. EP has the largest area and therefore the most analyte molecules, while CAT has the fewest. HT has a low area with a large error, but that is due to the fouling of the electrode mentioned above. In this technique the current represents the flux of reactants to the electrode surface, where the molecule is oxidized. Under identical flow conditions to the same electrode, the flux to the electrode is the same, and thus differences in cumulative oxidation current indicate another factor, such as electron transfer kinetics or availability of surface sites, is responsible to the differences in the measured current.

Figure 4c-d plot the peak height and full width at half maximum (FWHM) observed in the amperogram of each neurotransmitter. While the peak heights are similar, the FWHM of CAT is significantly smaller than the other analytes. The difference in FWHM is larger than the uncertainty associated with injection valve reproducibility. The peak narrowing indicates that CAT molecules are interacting at the electrode surface for a shorter period of time. Cyclic voltammograms of each species, Figure 5, shows that they all have oxidative and reductive peak separations (E_p) greater than 29.6 mV, indicative of thermodynamically irreversible reactions. The changes in FWHM indicate surface adsorption may be involved in the oxidation mechanism. HT does not display a cathodic peak, while CAT has the smallest peak separation. The results are consistent with previous reports.³⁷⁻³⁹

Modeling of Adsorption Dynamics

To further explore the SERS and electrochemical measurements, a model was developed with COMSOL Multiphysics to simulate both a continuous flow (Figure 6) and a finite injection of analyte (Figure 7) into the microchannel. These simulations capture the interactions between a fast moving sheath-flow and a sample eluting from the capillary wherein the analyte is focused onto an embedded 25 μm surface. The molecules can both adsorb and desorb based on a Langmuir adsorption model. In this model the adsorption coefficient, K , at equilibrium is proportional to the rate constants (k_{ads} and k_{des}) that govern adsorption to the surface.

$$K_{\text{eq}} = \frac{k_{\text{ads}}}{k_{\text{des}}}$$

Thus, by holding the adsorption constant we are able to vary K_{eq} systematically by changing the desorption value. Based on previous work where the adsorption dynamics of biogenic amines on a carbon fiber microelectrode were examined using fast-scan controlled-adsorption voltammetry, the adsorption value was set equal to 10 cm/s .¹⁹ This value also provides the best qualitative match to the adsorption rate observed in the experimental data. The rate of desorption was then altered to determine how the kinetics would change for different molecular structures. The parameters for the different modeled analytes are shown in Table 1.

Figure 6 presents the results of the COMSOL simulations with continuous flow where a sample stream of 1 mM analyte is introduced into the capillary at $t=0$ until an equilibrium surface concentration is reached. Figure 6a shows the results of a simulation at different times with a constant of desorption rate of 100 s^{-1} . The geometry is diagramed at $t=0$, highlighting the position of the inlet, capillary, SERS electrode, and outlet. The concentration in the channel at this time point is 0 mM. After, the flow of the 1 mM sample was initiated and the analyte was allowed to adsorb and desorb from the surface (Figure 6a, $t = 0.5, 1, 5, 10$, and 30 s). At $t = 30\text{s}$ and beyond it appears an equilibrium surface coverage has been reached.

The simulation was run with different rates of desorption to model how different analytes would interact with the surface (Table 1). Figure 6b presents the surface concentration versus time for each modeled analyte. The model with the slowest rate of desorption, analyte 1, has the highest equilibrium surface concentration while the one with the quickest, analyte 4 has the lowest.

The rates to reach equilibrium were determined by fitting each curve in Figure 6b to an exponential. The time constant, τ , of each model analyte is plotted in Figure 6c. The smaller the τ , the quicker the analyte appears and the values indicate that analyte 1 adsorbs at the quickest rate and analyte 4 at the slowest rate.

The previous model describes the system in a steady-state manner. While this accurately models the SERS experiment shown in Figure 2, the SERS injection and amperometry were

done by introducing a plug of analyte into the sample stream. To model this scenario an injection governed by a Gaussian pulse with a maximum concentration of 1 mM was introduced at some time point. The analyte plug interacts with the surface and then goes away, as illustrated in Figure 7.

Figure 7a shows the simulations with a rate constant of desorption of 100 cm/s at varying times. At $t=0$ the concentration in the channel is 0 mM, and remains there until the plug of analyte is introduced. During the injection (Figure 4a, $t=86, 100$, and 116 s), the analyte adsorbs and desorbs from the surface until it is all washed out of the channel ($t=150$ s).

The surface concentration on the surface at varying times for the different model analytes (Table 1) is shown in Figure 7b. The left and right plots show zoomed in views of the highlighted regions of the curve that appear to have different rates of desorption. The model with the slowest desorption rate, analyte 1, has the highest surface concentration while analyte 4 with the quickest desorption rate has the lowest.

The rate of adsorption and desorption was determined by fitting the highlighted portions of Figure 7b to an exponential and finding tau. Figure 7c shows the results. The tau for the on-rates are similar, as expected. However, the off-rates increase for the slower desorption rate constant. This indicates that the larger desorption rate constant, the longer it will adhere to the surface. Figure 7d confirms this by plotting the full width at half maximum (FWHM) for each model analyte. Analyte 1 has the largest FWHM, as well as the slowest rate of desorption, indicating that it adsorbs more readily to the surface.

Discussion

The combination of simulations with our experimental results provides insight into the role of absorption in SERS detection in flow as well as the oxidation mechanism of neurotransmitters. In both cases the interaction with the surface plays an important role. As seen with other studies,¹⁹ the data presented indicates these neurotransmitters exhibit different adsorption properties to the surface, and in-turn the signals obtained.

One outcome is an important observation on the role adsorption plays in the SERS response. The signal observed in a SERS experiment is an accumulation of a number of factors, a key one being the number of molecules interacting with the surface. Examining the analytes under the same conditions allows us focus in on the relationship between each neurotransmitter and the SERS surface. As seen in Figure 2 with continuous flow of analyte, HT demonstrates the largest S/N, while CAT the lowest. HT has been shown to have a higher K_{eq} than other neurotransmitters which dictates the strength of adsorption¹⁹ and suggests that more molecules are at the surface in the stronger adsorbing analyte, leading to a higher S/N in the SERS experiments.

Figure 6 shows the modeled analyte with the slowest rate of desorption, analyte 1, has the largest surface concentration and reaches equilibrium at the quickest rate. In turn, analyte 4 with the fastest rate of desorption has the lowest surface concentration. This demonstrates how K_{eq} influences the number of molecules at the surface and in-turn the SERS response. It

agrees well with the trend in S/N (Figure 2b) where the neurotransmitter with the strongest surface interaction, HT, has the largest signal.

The role of adsorption is further evident when examining the SERS injection results shown in Figure 3. As with continuous flow, HT not only has the highest signal (Figure 3b), but the largest peak width (Figure 3a) when looking at the SERS intensity profile of the largest Raman band during the injection. While DA also has a fairly broad peak, EP, NE, and CAT present blinking of the signal during the time the injection is passing through the focal volume. This behavior is indicative of stochastic detection and likely represents the fluctuation of molecules into hotspots at partial surface coverages. From a Langmuir model, we calculate the analyte coverage to be less than 1% of surface sites at the concentrations investigated. As SERS detection has been shown to be dominated by hotspots,⁴⁰ this suggests populating these sites is critical. The SERS efficiency of those analytes indicate a faster desorption mechanism that decreases the interaction time with the surface, decreasing the likelihood of occupying a hotspot during the injection. The decreased surface coverage is captured by the COMSOL model (Figure 7); however the model does not account for distribution of hotspots on the surface.

The amperometry measurements shed further light onto the surface interactions at the electrode. There is a strong qualitative agreement between the injection simulations and measured current, which provides additional insight into of each neurotransmitters interaction with the electrode surface. Figure 4 shows a comparison of successive injections of each analyte, including their peak height, peak area, and FWHM. HT demonstrated rapid fouling of the surface which indicates improved adsorption the surface. However, while DA, EP, NE, and CAT had similar peak heights, the FWHM of CAT was shorter than the other analytes. The reduced peak area indicates that fewer molecules are interacting with the electrode surface. Interestingly, the simulations show the same narrowing along with a decrease in surface concentration with the weaker adsorbing model analytes. As discussed above, the CV measurements indicate irreversible electron transfer reactions. This suggests adsorption is key step in the oxidation mechanism. The SERS measurements show no signal at oxidized potentials, which is consistent with the oxidized species having poorer affinity for the surface. Only in the case of HT, which shows fouling behavior are peaks observed at these potentials.

Conclusions

The combination of *in situ* SERS and amperometry measurements with finite element simulations provide new insight into the role of adsorption for the detection and characterization of neurotransmitters and other analytes. Our results indicate that molecules with the highest surface affinity show the strongest SERS signals. Additionally, our results show that adsorption is a key intermediate in the oxidation of neurotransmitters on gold surfaces. Overall, these results illustrate the importance of surface adsorption for *in situ* characterization of molecules.

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Dopamine

Catechol

Epinephrine

Norepinephrine

The molecular structure of the oxidized (right) and reduced (left) species of each neurotransmitter is shown here.

Figure 2. A comparison of the SERS response of each neurotransmitter under the same conditions at open circuit potential. (a) Shows the average spectrum observed over a 2 s period in the continuous flow experiment. (b) The peak height of the most intense band in each was measured and the signal-to-noise ratio for each neurotransmitter was calculated.

Figure 3.

(a) SERS intensity profile of the largest Raman band for each neurotransmitter (Figure 3b) at open circuit potential is plotted against time. (b) Shows an average spectrum of each analyte during the injection.

Figure 4.

Amperometric analysis of 5-HT, DA, NE, EPI, and CAT. (a) Shows the current versus time curves for consecutive injections of each neurotransmitter. The right panel compares the (b) peak area, (c) peak height, and (d) FWHM for each analyte.

Figure 5.
Cyclic voltammograms for each neurotransmitter on the deposited Au microelectrode.

Figure 6.

COMSOL simulations were done to assess how analytes with different surface affinities will interact with the microelectrode in the channel. (a) The results of a simulation from model analyte 3 are shown at different time (0, 0.5, 1, 5, 10, and 30s). (b) Shows a plot of the surface concentration versus time for the four model analytes with different desorption coefficients. Analyte 1, with the slowest desorption, has the highest equilibrium surface concentration. The rate was determined by fitting the curves to an exponential and finding the time constant, tau. (c) Demonstrates the different rates of each analyte.

Figure 7.

COMSOL simulations were done to model a plug of analyte being introduced into the channel and allowed to adsorb and desorb from the surface. (a) The results of a simulation from model analyte 3 are shown at different time points (0, 86, 100, 116, and 150 s). Shows a plot of the surface concentration versus time for the four model analytes with different desorption coefficients (Table 1). The left and right show zoomed in views of the highlighted regions of the curve. (c) The time constant, τ , was determined by fitting the highlighted portions to determine the on- and off-rate for each modeled analyte. These results indicate different rates of decay. (d) Shows the full width at half maximum of the curve for each analyte.

Table 1
Parameters used for the analytes modeled in COMSOL Multiphysics

Modeled Analyte (1 mM)	Kads (cm/s)	Kdes (1/s)
Analyte 1	10	50
Analyte 2	10	75
Analyte 3	10	100
Analyte 4	10	125

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