Surface-Enhanced Raman Spectroscopy of Benzenethiol Adsorbed from the Gas Phase onto Silver Film over Nanosphere Surfaces: Determination of the Sticking Probability and Detection Limit Time

Kevin B. Biggs, Jon P. Camden, Jeffrey N. Anker, and Richard P. Van Duyne

J. Phys. Chem. A, 2009, 113 (16), 4581-4586 • DOI: 10.1021/jp8112649 • Publication Date (Web): 16 March 2009

Downloaded from http://pubs.acs.org on May 14, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
A chemical warfare agent (CWA) gas detector based on surface-enhanced Raman spectroscopy (SERS) using robust nanostructured substrates and a portable Raman spectrometer is a promising alternative to existing modalities. A gas-dosing apparatus was constructed to simulate chemical gas exposure and provide a platform for quantitative analysis of SERS detection. As a first step toward characterizing SERS detection from the gas phase, benzenethiol (BT) has been chosen as the test analyte. SERS spectra were monitored during BT adsorption onto a silver film over a nanosphere (AgFON) substrate. The SERS detection limit time (DLt) for BT on a AgFON at 356 K is found to be 6 ppm-s (30 mg-s m⁻³) for a data acquisition time (t_acq) of 1 s. The DLt for this kinetically controlled sensor is fundamentally determined by the low sticking probability of BT on AgFONs which is determined to be ~2 × 10⁻² at 356 K. The sticking probability increases with increasing temperature consistent with an adsorption activation barrier of ~13 kJ mol⁻¹. Although the DLts found in the present study for BT are in the low ppm-s, a theoretical model of SERS detection indicates DLts below 1 ppb s⁻¹ for t_acq = 1 s are, in fact, achievable using existing portable Raman instrumentation and AgFON surfaces. Achieving this goal requires the sticking probability be increased 3 orders of magnitude, illuminating the importance of appropriate surface functionalization.

Figure 1. The localized surface plasmon resonance of a AgFON surface optimized for SERS with 785 nm laser excitation wavelength.
Experimental Methods

Materials. All chemicals were reagent grade and used as received. Oxygen-free high-conductivity copper was obtained from McMaster-Carr (Chicago, IL) and cut into 18 mm diameter disks. Survfactant-free, silica nanosphere suspensions (600 nm ± 20 nm 10% solid) were purchased from Interfacial Dynamics. Ultrapure water (18.2 MΩ cm⁻¹) from a Millipore system (Marlborough, MA) was used for substrate and solution preparation. Silver wire (99.99%) was purchased from Kurt J. Lesker Co. BT was purchased from Aldrich (Milwaukee, WI). NH₄OH and H₂O₂ were purchased from Fisher Scientific (Fairlawn, VA) and CH₃CH₂OH from Pharmco-AAPER and used for cleaning.

AgFON Fabrication. Copper substrates were cleaned by sonication (1510 Branson ultrasonicator) in 10:1:1 H₂O:30% H₂O₂:NH₄OH. Ten microliters of nanosphere solution was dropsonication (1510 Branson ultrasoundator) in 10:1:1 H₂O:30% H₂O₂:NH₄OH (7 torr) over the nanosphere-covered surface using a thermal vapor deposition system (home-built). The Ag mass thickness (fwhm) of Ag bonds (7.4 kJ mol⁻¹) was used to record SERS spectra. Excitation is achieved from the minimum in a baseline region. A conversion factor, Z, is calculated by modification of eq 1 to account for the observed irreversible binding of half-mustard gas to the AgFON substrate. Furthermore, BT has a large UV absorption cross-section which provides a convenient means for monitoring its concentration in the gas phase by UV−vis spectroscopy.

Figure 2. Gas-phase dosing apparatus.

Figure 3. UV spectra of BT gas acquired during dosing.

Dosing. Gas dosing is achieved by mass flow-controlled (MKS, M100BO1312CR18B) mixing of BT saturated N₂ with pristine N₂ (Figure 2). The saturated BT carrier gas is passed at 1 mL min⁻¹ through a bubbler containing neat BT and is later diluted downstream at 100 mL min⁻¹. BT concentration is monitored by UV−vis spectroscopy (Figure 3). Once the BT concentration reaches steady state, the gas stream is allowed to flow over the SERS substrate by opening the back valve on the sample cell and then simultaneously opening and closing the front and vent valve, respectively. Only ultradry grade N₂ was used. All piping is 0.25 in. stainless steel except the sample cell which is 0.125 in. All connections are made with standard Swagelock or VCR fittings.

Temperature Control. A Peltier solid-state thermoelectric cooler (Melcor, CP 1.0−31−05 L) controlled by a Melcor MTTC-1410 temperature controller (±0.004 C) was used for temperature control. A temperature sensor (Melcor, 2-wire PT1000 RTD) in contact with a copper cylinder (length 8 mm diameter 10 mm) clamped between the TEC and substrate provide temperature feedback. Silicon-based grease (Radio Shack) was applied at the TEC/copper cylinder junction and copper cylinder/substrate junction.

Analysis. Spectra were stored on a hand-held computer. All spectra were processed with Matlab scripts which calculated the peak intensities by subtracting the maximum peak height from the minimum in a baseline region. A conversion factor, C, was determined for converting SERS intensities recorded in adu mW⁻¹ s⁻¹ to photons detected using benzene (BZ) as a standard and the general expression:

$$I(\omega) = I(\omega_0)N \frac{d\sigma(\omega_0)}{d\Omega} Z$$

where I(\omega_0) is the Raman scattering intensity at \(\omega_0\), I(\omega) is the incident laser intensity at \(\omega_0\), N is the number density of scattering, \(d\sigma(\omega_0)/d\Omega\) is the Raman cross-section at \(\omega_0\), and Z is a geometric factor that takes into account the spectrometer depth of field. C is calculated by modification of eq 1 to account for acq and some experimental parameters:
$C = I(\omega_s)N_{BZ}\frac{d\sigma_{BZ}(\omega_s)}{d\Omega} - I_{acq} \Omega T_c T_s Q(\omega_s)N_{BZ}^{\text{RBT}}(\omega_s)^{-1} \int I_{acq}^{\text{RBT}}(\omega_s, z) dZ$ (2)

where $(d\sigma_{BZ}(\omega_s))/d\Omega$ is the BZ Raman cross-section ($4.9 \times 10^{-36} \text{ cm}^2 \text{ sr}^{-1} \text{ molecules}^{-1}$ at $\omega_s = 992 \text{ cm}^{-1}$) and $I_{acq}^{\text{RBT}}(\omega_s)$ is the BZ Raman scattering intensity (adu mW$^{-1}$ s$^{-1}$) at $\omega_s$. The geometric factor, $fI_{acq}^{\text{RBT}}(\omega_s, z) dZ$, was determined by collecting a series of BT SERS spectra on an AgFON at $\omega_s = 1076 \text{ cm}^{-1}$, as a function of focal distance, $z$ (150 $\mu$m steps, Line Tool Co. Model A RH micro positioning stage). Normalization and integration of peak intensities yields $z = 0.12 \text{ cm}$. The conversion factor was determined to be 32 photons mW$^{-1}$ s adu$^{-1}$.

The Raman cross-section of BT, $(d\sigma_{BT}(\omega_s))/d\Omega$, at $\omega_s = 1091 \text{ cm}^{-1}$ (mode responsible for SERS at 1076 cm$^{-1}$) was determined to be $6.4 \times 10^{-31} \text{ cm}^2 \text{ sr}^{-1} \text{ molecule}^{-1}$ by comparison with the known BZ Raman cross-section using the relation:

$$\frac{d\sigma_{BT}(\omega_s)}{d\Omega} = \frac{I_{acq}^{\text{RBT}}(\omega_s') \times N_{BZ}}{N_{BT} \times I_{acq}^{\text{BZ}}(\omega_s)}$$ (3)

where $I_{acq}^{\text{BZ}}(\omega_s)$ is the Raman scattering intensity of neat BT at $\omega_s$.

Results and Discussion

An important property of this gas-phase SERS study is that BT binds irreversibly to the SERS substrate through a strong S–Ag bond. Similarly, many CWAs can irreversibly bind to silver or chemically functionalized silver surfaces, and the S–Ag bond is likely responsible for the observed irreversible binding of mustard gas to the AgFON substrate. As a result of irreversible adsorption, detection here is characterized, not by a limit of detection, but by a detection limit time (DLt) dependent on the kinetic rate of analyte adsorption. Lower concentrations can be detected for longer exposure periods, and the DLt is defined as the minimum concentration that can be detected in one second of exposure for a $t_{acq} = 1 \text{ s}$ and spot size of $1.4 \times 10^{-5} \text{ cm}^2$. This study seeks to discover how quickly molecules can be detected by SERS and how it might be accelerated.

To quantitatively characterize SERS gas detection, the SERS signal arising from 8 ppm (40 mg m$^{-3}$) BT gas in N$_2$ dosed to a AgFON maintained at 358 K was continuously monitored with a portable Raman instrument (Figure 4A). A comparison of the SERS and normal Raman spectra of BT is shown in Figure 4B, with slight deviations in peak position highlighted. Shifts in peak position are commonly observed in SERS and arise from differences in the chemical environment experienced by the bound and neat species. Differences in relative SERS and normal Raman peak intensities are attributed to preferential enhancement of vibration modes oriented perpendicular to the surface.$^{45,47,48}$

The temporal evolution of the BT SERS intensity at 1076 cm$^{-1}$ is shown in Figure 5A. The DLt here is determined by analyzing the background noise prior to chemical dosing and assessing when a measurable SERS signal is observed. The initial rate of adsorption is illustrated by the slope of the red line in Figure 5A, determined by a linear regression fit to the first four data points in the linear regime of the adsorption uptake curve, yielding $k = 8.2 \times 10^4 \text{ photons s}^{-1}$ ($R^2 > 0.999$). This slope can be easily converted into a rate of molecular adsorption, $k_{ads}$, through the following expression:

$$k_{ads} = \frac{k \cdot N}{N_{P, sat}(\omega_s)}$$ (4)

where $N$ is the surface number density ($\sim 6.8 \times 10^{14} \text{ molecules cm}^{-2}$ on flat Ag surfaces),$^{49}$ $A$ is the AgFON surface area excited...
The sticking probability is the chance a molecule that collides with the substrate adsorbs. In characterizing the DT the value of the sticking probability is most important in the initial linear regime of adsorption, where the number of unoccupied sites are much greater than the number of occupied and adsorption occurs at a constant rate. A comprehensive model for determining the total SERS intensity detected based on this initial sticking probability has been previously formulated. Incorporating the known parameters for the experimental setup used in this work and generalizing this model for the analyte Raman cross-section and the number of SERS photons detected at \( \omega_e \), \( N_\rho(\omega_e) \), can be expressed through the following relation during the initial linear regime of adsorption:

\[
N_\rho(\omega_e) = 1.0 \times 10^{35} \text{ (molecules \times photons \times sr \times cm}^{-2} \times \text{torr}^{-1} \times s^{-2}) \frac{d\rho(\omega_e)}{d\Omega} P_1 t_{\text{exp}} t_{\text{acq}} S_{\text{EF}}(\omega_e) \tag{5}
\]

where \( P_1 \) is the partial pressure, \( t_{\text{exp}} \) is the chemical gas exposure time, \( S_i \) is the initial sticking probability, and \( EF(\omega_e) \) is the enhancement factor at \( \omega_e \) (~10^4 for the AgFON at 1076 cm\(^{-1}\)).

Increasing the sticking probability may be achieved by modifying the surface to increase the interaction of the analyte with the surface. For this method to succeed, it will be important to systematically study the activation barriers to adsorption, for example by varying the substrate temperature. A fourth potential method is to ionize the analyte and use electric fields to direct the ions to the sensing region. Finally the DT can be improved by increasing the signal-to-noise ratio through improvements in the spectrometer, substrate, and signal analysis. It is also apparent from eq 5 that \( N_\rho(\omega_e) \) is directly proportional to enhancement factor. Model calculations predict SERS enhancement factors can reach values of \(~10^{11}\) in the junctions between nanoparticle dimers. SERS active sites with an \( EF(\omega_e) \) of \(~10^{11}\) covering 10% of the substrate surface could increase the number of photons detected independent of any increase in the kinetics of the adsorption process. In addition, the signal-to-noise ratio could be increased by addition of an appropriate SERS reference standard, which could be added through controlled gas-phase adsorption of a fraction of a monolayer.

The Raman cross-sections of several CWAs and CWA simulants have been measured by Christesen and show strongest lines on order \( 10^{-30} \text{ cm}^2 \text{sr}^{-1} \text{molecule}^{-1} \) (at 785 nm excitation). These Raman cross-sections are greater than that of the analyte Raman scattering cross-section observed upon adsorption to a SERS substrate.

The sticking probability for organothiol adsorption on noble metal surfaces has been shown to range from unity to \(~10^{-8}\) to \(~10^{-5}\). The initial sticking probability, \( S_i \), is expressed as a ratio of the initial adsorption rate to the BT collision frequency, approximated using ideal gas kinetics:

\[
S_i = k_{\text{ads}} \sqrt{2\pi MRT/PAN_\lambda^{-1}} \tag{6}
\]

where \( M \) is the molar mass, \( R \) is the ideal gas constant, \( T \) is the temperature of the dosed gas, and \( N_\lambda \) is Avogadro’s number. Using eq 6 the BT sticking probability is calculated to be \(~1.5 \times 10^{-5}\) (the BT surface collision rate is \( 3.7 \times 10^{13} \) molecules \( \text{cm}^2 \times \text{torr}^{-1} \times s^{-2} \)).

Substitution of this sticking probability in eq 5 predicts \( N_\rho(\omega_e) = 8.2 \times 10^8 \) photons following a \( t_{\text{exp}} = 1 \) s of 8 ppm BT with \( t_{\text{acq}} = 1 \) s. Changing \( S_i \) to 0.01, a 3 orders of magnitude increase, increases \( N_\rho(\omega_e) \) to \( 5.6 \times 10^7 \) photons, requiring only \( t_{\text{exp}} = 1 \) ms for positive detection. A \( S_i \) of unity would decrease the DT from the 6 ppm-s demonstrated here to 90 ppt-s with \( t_{\text{acq}} = 1 \) s.

Equations 5 and 6 suggest at least five methods to increase the adsorption kinetics and otherwise improve the DT. One method is to increase the collisions frequency by artificially increasing the pressure of the gas being analyzed. It is expected that the collision rate may be increased by 3 orders of magnitude without excessive difficulty (for example 100–1000 atm pressure is often used in high performance liquid chromatography columns). A second method, commonly employed in GC, is to increase the concentration of analyte with the use of cold traps or solvent traps, and then flow a concentrated gas stream over the sample. A third method is to increase the sticking probability. Increasing the sticking probability may be achieved by modifying the surface to increase the interaction of the analyte with the surface. For this method to succeed, it will be important to systematically study the activation barriers to adsorption, for example by varying the substrate temperature. A fourth potential method is to ionize the analyte and use electric fields to direct the ions to the sensing region. Finally the DT can be improved by increasing the signal-to-noise ratio through improvements in the spectrometer, substrate, and signal analysis. It is also apparent from eq 5 that \( N_\rho(\omega_e) \) is directly proportional to enhancement factor. Model calculations predict SERS enhancement factors can reach values of \(~10^{11}\) in the junctions between nanoparticle dimers. SERS active sites with an \( EF(\omega_e) \) of \(~10^{11}\) covering 10% of the substrate surface could increase the number of photons detected independent of any increase in the kinetics of the adsorption process. In addition, the signal-to-noise ratio could be increased by addition of an appropriate SERS reference standard, which could be added through controlled gas-phase adsorption of a fraction of a monolayer.
where $A$ is the pre-exponential factor and $E_a$ is the activation energy. The slope yields an activation energy barrier of 13 kJ mol$^{-1}$. This activation energy is comparable with those measured by Dubois et al. for the chemisorption of ethanethiol and methanethiol gas on Au ($21-29$ kJ mol$^{-1}$). It is hypothesized that this activation energy is required for organothiol dissociative attachment (RSH + Au $\rightarrow$ RS/Au + $1/2$H$_2$). Further evidence of a dissociative attachment mechanism is in the disappearance of the of S–H in-plane bending vibrational mode located at 918 cm$^{-1}$, absent in the SERS spectra (see Figure 4B). Contrary to the work of Dubois et al. and Eberhardt et al. with alkanethiol adsorption on Au(111), the data here does not indicate any physisorbed precursor state where the RSH remains intact on the surface before dissociation. It is unclear whether this difference in observed BT surface chemistry is related to a difference in the AgFON morphology compared with the of flat single crystal Au(111) surfaces used in these studies or whether the kinetics of BT adsorption differs from that of alkanethiol.

An unexpected, double-humped feature is apparent in the 297 and 260 K data sets, where an abrupt deviation from Langmuir kinetics is observed and BT exhibits presaturation increases in sticking probability (Figure 6B,C). Such adsorption dynamics have not been observed for alkanethiol adsorption from the gas phase on flat Au surfaces, and more work is needed to understand the physical nature behind these features.

Conclusions

The results presented represent a significant step toward the real-time gas detection of CWAs with portable SERS instrumentation. A study of BT gas-phase adsorption on AgFONs provides an instructive system for studying the limits of gas-phase SERS detection. The DLt’s were determined by comparing the early temporal evolution of the BT SERS signal with respect to the background signal prior to dosing using $t_{aq} = 1$ s. The SERS DLt for BT on a AgFON at 356 K is projected to be 6 ppm-s, with accumulation of analyte during extended exposure periods enabling detection of lower concentrations. The calculated initial sticking probability of $\sim 2 \times 10^{-2}$ for this system indicates the greatest improvements in SERS DLt’s below 1 ppb-s, will be achieved through increases in adsorption kinetics. The initial BT/AgFON sticking probability is found to be strongly temperature dependent with an activation barrier of $\sim 13$ kJ mol$^{-1}$. The quantitative nature of these experiments has provided insight into the potential use of SERS as a gas-phase detection modality. Looking toward the future, highly enhancing SERS substrates with optimized surface/analyte affinities are poised to play an increasingly important role in areas where robust, sensitive, and affordable sensing is required.

Acknowledgment. The authors gratefully acknowledge support from the National Science Foundation (ECC-0647560, CHE-0414554, BES-0507036), the DTRA JSO Program (FA9550-06-1-0558), AFOSR/DARPA Project BAA07-61 (FA9550-08-1-0221), and the NSF MRSEC (DMR-0520513) at the Materials Research Science and Engineering Center of Northwestern University, and a Ruth L. Kirschstein National Research Service Award (5 F32 GM077020) to J.N.A.

References and Notes
