Investigation of the Adsorption of Gaseous Aromatic Compounds at Surfaces Coated with Heptakis(6-thio-6-deoxy)- β -cyclodextrin by Surface-Enhanced Raman Scattering

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Heptakis(6-thio-6-deoxy)- β -cyclodextrin (TCD) was prepared and chemisorbed at the surface of rough silver substrates for surface-enhanced Raman scattering (SERS). The enhanced adsorption of methyl orange and the stability of its azo form at the TCD-coated substrates proved the capability of the immobilized TCD to form inclusion complexes with organic guest molecules. This complexation was used for the detection of aromatics in the gas phase. Toluene, ethylbenzene, *m*-xylene, chlorobenzene, and *m*-dichlorobenzene were strongly adsorbed at the TCD-coated substrates, thus making possible the detection of low concentrations, as for example 15 ppm of *m*-dichlorobenzene. Benzene was weakly adsorbed and detectable in high concentrations only. Since the strongly adsorbed aromatics desorb very slowly, TCD-coated substrates may be applicable for the detection of slowly changing concentrations or as integrating sensors in the surveillance of chemical exposures. The capability of immobilized TCD to adsorb also polycyclic aromatic hydrocarbons was demonstrated using naphthalene.

Introduction

Submonomolecular layers of adsorbed molecules at rough metal surfaces can easily be detected and characterized by surface-enhanced Raman scattering (SERS). The SERS method became attractive for the development of chemical sensors because of this high sensitivity and because of recent improvements in the instrumentation.

Most chemical sensors measure properties such as refractive index, mass, or fluorescence intensity, which are rarely specific for the substances to be detected. Chemical selectivity of sensors is mainly achieved by coating appropriate surfaces with certain adsorbing or reacting substances. In case these coatings interact with different adsorbates, the performance of the corresponding sensors is seriously affected by cross-sensitivities. Additional efforts such as recognition of adsorption patterns at differently coated sensors forming an array are often necessary to improve the selectivity. These measures increase considerably the technical requirements and introduce new uncertainties, for instance, drift phenomena of the signal patterns.

SERS provides vibrational spectra, which are quite characteristic of the detected molecules and which can be used for their reliable identification by comparison with reference spectra. Therefore, SERS offers the capability for chemical multisubstance sensing because the interesting analytes that are adsorbed at a coating can be identified by their vibrational spectra.

This concept has been successfully demonstrated for the detection of aromatics in water and in the gas phase at substrates coated with *p-tert*-butylcalix[4]arenetetrathiol (BCAT).^{1,2} The aromatics were fully reversibly adsorbed at BCAT-coated SERS substrates, and therefore, the SERS intensities from these substrates gave a measure of the present bulk concentrations of the aromatics. The limits of detection were comparatively high, which was probably due to low adsorption enthalpies.¹ The BCAT cone is actually somewhat too narrow for an optimum

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inclusion of aromatic compounds. Quantum chemical simulations have shown that BCAT most probably adsorbs the aromatics between the *tert*-butyl groups and not deep in the cone.³ Therefore, larger cone- or cage-shaped recipients are badly needed as sorbents for aromatics or even larger molecules. Unfortunately, completely substituted thiol derivatives of larger calixarenes are difficult to synthesize up to now.⁴

Another type of cone-shaped molecules, the cyclodextrins, can also be used as receptors on the surface of chemical sensors. Cyclodextrins exhibit larger cavities with different dimensions, and their primary hydroxyls are more reactive and thus easier to be chemically modified than the phenolic OH groups of calixarenes. The cavities of the cyclodextrins are hydrophobic and capable of forming inclusion complexes with a wide range of guest compounds, such as acids, ions, halides, aliphatic, alicyclic, and aromatic hydrocarbons.^{5–8} Thiolated cyclodextrins have been immobilized on gold and silver surfaces and characterized by SERS⁹ and surface plasmon spectroscopy.¹⁰

In the present paper, heptakis(6-thio-6-deoxy)- β -cyclodextrin (TCD), a multithiolated derivative of β -cyclodextrin (CD), was prepared, immobilized at silver substrates, characterized by SERS, and used for the adsorption of gaseous mono- and bicyclic aromatics.

Experimental Section

Chemicals. Zinc powder (purum), methanesulfonyl chloride (puriss., $\geq 99\%$), bromine (puriss.), CD (purum, $\geq 99\%$ HPLC), potassium thioacetate (purum, $\geq 98\%$), *N*,*N*-dimethylformamide (DMF: puriss., $\geq 99.5\%$ GC; anhydrous, H₂O = 0.01%) and methanol (puriss., $\geq 99.5\%$; anhydrous, H₂O = 0.01%) were supplied by Fluka. Chloroform ($\geq 99\%$) was supplied by Merck. High-purity water with an electrical conductivity below 0.07 μ S/cm was produced by a commercial water purification system (Millipore Milli-Q) equipped with an additional filter for organics. Potassium thioacetate was recrystallized twice in water to remove fluorescent impurities.



Figure 1. Structure and dimensions of the TCD molecule.



Figure 2. Scheme of the reaction pathway of the TCD preparation.

Chemical Preparations. TCD (Figure 1) was prepared from CD via its bromine and thioacetate derivatives (Figure 2). Methanesulfonyl bromide CH₃SO₂Br was freshly prepared from methanesulfonyl chloride, zinc powder, and bromine as described by Sieber.¹¹ Composition and purity of the vacuum-distilled product were confirmed by mass spectrometry. Heptakis-(6-bromine-6-deoxy)- β -cyclodextrin (BrCD) was prepared from CD and methanesulfonyl bromide according to the procedure described by Takeo.¹²

The TCD was prepared from BrCD along a reaction pathway similar to that proposed by Chung¹³ but with some modifications of the procedure: 0.9 g of potassium thioacetate were dissolved in 10 mL of DMF. This solution was added dropwise at room temperature and under nitrogen atmosphere to a stirred solution of 1.7 g of dry BrCD in 30 mL of DMF. After further stirring for 24 h, the yellowish solution was poured into a stoichiometric amount of 5% KOH in methanol and stirred for 5 h at 40 °C under a nitrogen atmosphere. Some product precipitated during the addition of the methanolic solution and during stirring. The suspension was then cooled in ice water, mixed under steady cooling with 100 mL of ice water, and neutralized with small quantities of 2 M HCl. The resulting mixture was stored overnight in a refrigerator and then centrifuged. The precipitate was cleaned twice by washing with small amounts of pure water and centrifugation. The product was dried for 5 days at room temperature in a vacuum over P₄O₁₀. CD, BrCD, and TCD were characterized by NMR spectroscopy.

Preparation of Substrates. SERS substrates were prepared by spin-coating glass slides with 150 μ L of a 5% aqueous suspension of 0.3 μ m alumina particles according to a method described by Bello et al.¹⁴ A chromium layer with a thickness of 2 nm was evaporated in a vacuum onto the substrates to improve the adhesion between glass and silver. A silver layer with a thickness of 75 nm was evaporated immediately after the deposition of chromium. TCD-coated substrates were generated by immersion of metal-coated slides into 0.8 mM aqueous solutions of TCD for 2 h. After being coated with the TCD, the substrates were rinsed with pure water, and then immersed for 10 min in a 10 mM aqueous solution of KI, which is known to increase the SERS intensities by an additional "chemical" enhancement.¹⁵ After being rinsed with water and dried, the slides were ready for use.

Preparation of Test Gas Mixtures. Schemes of the measuring cell for time-resolved investigations and of the apparatus used for test gas generation and flow control were published elsewhere.² Special care was taken to avoid contact of the test gases with materials other than stainless steel and glass. Gaseous nitrogen with 99.999% purity was produced by evaporation of liquid nitrogen. After pressure reduction, traces of water and organic impurities were removed by molecular sieve and activated carbon filters. Then the carrier gas stream passed a flow controller operating down to flow rates of 1 mL/min. A four-port valve (Valco C4WP) allowed the gas to flow either directly to the measuring cell or through a glass flask for evaporation of aromatic substances. The 280 mL evaporation flask was equipped with a septum for the injection of liquid aromatics and contained a glass-coated magnetic stirrer for continuous mixing of the gas. The gas concentrations were calculated according to the ideal gas equation for the actual room temperature of 25 °C, assuming complete evaporation of the liquids and uniform mixing of the vapors with the carrier gas. A soap bubble flow meter was used to measure flow rates downstream the measuring cell. Gas lines connecting the valve, flask, and cell had an overall length of 10 cm and an inner diameter of 1 mm.

The development of the gas concentrations after switching the valve was controlled by placing a photoionization detector (PID) downstream the measuring cell. A few seconds after opening the evaporation flask, the aromatics reached the PID, leading to about 80% of the final signal within 2 s and developing the full signal within 5-10 s. This delay can be neglected, considering the integration time of SERS measurements of 1 min. The decrease of concentrations was also controlled by the PID. The decay was similarly fast as the increase, and no noticeable desorption from cell materials could be observed. It should be mentioned that worse results were obtained using a cell made essentially of Teflon. The low concentrations of test gases applied in the determination of the limits of detection were produced in separate glass flasks by two dilution steps. First, $10-100 \ \mu$ L of a liquid aromatic substance was injected with a microliter syringe through a septum into a first glass flask with a volume of 1.127 L and evaporated there under constant stirring with a glasscoated magnetic stirrer. With a second syringe proper amounts of the gas from the first flask were injected into a second flask with a volume of 1.124 L. The gas in the second flask was also stirred.

NMR Spectroscopy. All NMR measurements were carried out on a JEOL-GX-400 NMR spectrometer equipped with a 5 mm $^{13}C^{-1}H$ dual probe-head. Measurement frequencies were 400 MHz for ¹H and 100 MHz for ¹³C. Spectral widths of 5 and 24 kHz were used for the one-dimensional ¹H and ¹³C spectra, respectively. A quantity of 32K data points were acquired for ¹H and ¹³C spectra. Exponential broadenings of 0.31 and 1.47 Hz were applied to the free induction decays (FIDs) prior to the Fourier transformation for ¹H and ¹³C spectra, respectively. Absolute value two-dimensional ¹H–¹H-correlated (COSY) spectra and ¹³C–¹H-correlated (HETCOR) spectra were acquired using standard pulse sequences.

COSY. The spectral width was 2.1 kHz in both dimensions; 1024 data points in F_2 and 512 data points in F_1 were acquired with subsequent zero filling to 1K in the second dimension. An unshifted sine filter was applied in both dimensions prior to the Fourier transformation.

HETCOR. Spectral widths of 2.1 kHz for ¹H and 11 kHz for ¹³C were used. Quantitites of 4K data points in F₂ and 256 data points in F₁ were acquired with subsequent zero filling to 8K in F₂ and 512 points in F₁. Prior to the Fourier transformation, an exponential window of 2.7 Hz line broadening and an unshifted sine window were applied in F₂ and F₁, respectively. The delay times $\tau = 3.57$ ms and $\delta = 1.80$ ms were adjusted to a ¹*J*(C,H) coupling constant of 140 Hz.

Assignment of the ¹H chemical shifts was obtained from COSY analysis, starting with the anomeric H_1 proton signal that was easily identified because of the absence of a second COSY correlation signal and the high ¹³C chemical shift value of its HETCOR cross-peak. The HETCOR spectrum was then used to correlate ¹H assignments with ¹³C shifts in a straightforward manner.

SERS Measurements. SERS spectra were taken with a DILOR *XY* triple monochromator with subtracting dispersion of the first two stages. A CW Ti:sapphire laser (Coherent 890) operating at a wavelength of 702 nm served as the excitation source. The laser radiation was filtered by a grating monochromator for removal of spontaneous emission background. A Wright Instruments nitrogen-cooled CCD camera with a 298 × 1152 pixel EEV 88131 chip served as a detector. The Raman spectra were measured in backscattering geometry using *f*/1.0 collection optics. To prevent heating of the surface, which might cause desorption of adsorbates or degradation of SERS substrates, a cylinder lens with *f* = 200 mm was used to generate a line focus with a length of 300 μ m and a width of 30 μ m at the substrate. The laser power at the sample was about 50 mW.

Results and Discussion

Preparation of TCD. BrCD was obtained in a yield of 75% as a white, water-insoluble powder, which was soluble in pyridine and DMF: mp ~180 °C (decomp), $[\alpha]_D +100^\circ$ (*c* 1, DMF) (lit.: mp 205–206 °C decomp, $[\alpha]_D +98^\circ$ (*c* 1, pyridine),¹² Beilstein test for halogen strongly positive. TCD was obtained in a yield of 22% as a white-grayish powder, which

TABLE 1: Proton and ¹³C NMR Shifts (ppm) of β -Cyclodextrin and Its Derivatives

	H_1	H_2	H_3	H_4	H_5	H _{6a}	ı/b	SH
CD BrCD	4.83 4.98	3.28 3.37	3.63 3.65	3.34 3.34	3.55 3.83	3.63 4.01/3	3.65	2.10
ICD	4.92	3.34	3.60	3.33	3.66	3.18/2	2.77	2.10
	C_1	Ca	2	C ₃	C_4	C5	C ₆	
CD	102.0	72.	2 7	2.9	81.3	71.8	59.7	,
BrCD TCD	102.0 102.0	71. 72.	9 7 1 7	2.0 2.4	84.5 84.8	70.9 71.9	34.1 25.7	,

was sparingly soluble in water and soluble in pyridine and DMF: mp \sim 270–280 °C (decomp), $[\alpha]_D$ +90° (*c* 1, DMF), Beilstein test negative. The most delicate issue of the preparation was to avoid hydrolysis. The high pH during the cleavage of the thioester led apparently to strong hydrolysis of the cyclodextrin skeleton if the reaction was performed in water as proposed elsewhere.¹³ Cleavage of the thioester in anhydrous methanol increased the yield significantly.

Proton and ¹³C NMR shifts of CD, BrCD, and TCD are listed in Table 1. The measured NMR shifts for CD are in good agreement with literature data.¹⁶ Considerable shifts of H₆ and C₆ signals after the preparations and weak influences on the other shifts confirm the desired selective substitution of the primary hydroxyls and the conservation of the cyclodextrin skeleton. The location of the thiol groups is further confirmed by the appearance of H_{6a/b}-SH cross-peaks and the absence of other cross-peaks of the SH signal in the ¹H-¹H-correlated twodimensional spectrum. The ¹³C shifts of C₆ were lowered by 25.6 ppm owing to substitution of OH by Br and by 8.4 ppm owing to substitution of Br by SH. Both values agree well with literature data for alkanes (28.3 and 8.9 ppm, respectively¹⁷) and thus confirm the desired type of substitution. The ratio of the integrals of the SH signal and the anomeric (H_1) proton signal in the one-dimensional proton NMR spectrum was found to be 1.1:1.0, which shows that every glucose unit carries an SH substituent. The ¹H NMR spectra of BrCD and TCD showed that these samples also contained DMF with signals at 2.71 and 2.89 ppm. The integral ratio of the fairly well isolated NMR signals of the H₁ protons and the DMF signal at 2.89 ppm was, after correction for the different numbers of protons per molecule, 1.00:1.07. For BrCD, the analogous ratio was 1.15: 1.00. Both these findings account for a TCD/DMF ratio close to unity. Since physisorbed DMF was certainly removed during the vacuum-drying, there remained probably 1:1 inclusion complexes of BrCD or TCD on the one hand and DMF used as solvent during the preparation on the other hand. This inclusion confirmed the preservation of complexing capabilities of the CD after derivatization.

Raman spectra of CD, BrCD, and TCD are shown in Figure 3. The spectrum of CD exhibits CH_x stretching bands around 2900 cm⁻¹ and numerous bands in the fingerprint region, which cannot be assigned unambiguously. The spectrum of BrCD exhibits two strong bands at 615 and 683 cm⁻¹, which is in the expected range for C–Br stretching vibrations in two different conformations.¹⁸ The spectrum of TCD does not show any C–Br stretching bands but a strong S–H stretching band at 2574 cm⁻¹. The band at 667 cm⁻¹ in the TCD spectrum may be related to the C–S stretching vibration; however, a definite assignment is not possible, since this band is close to one of the strongest bands of DMF being also present in the sample.

Both NMR and Raman data gave strong evidence for the quantitative occurrence of the desired substitutions and the successful preparation of TCD.



Figure 3. Raman spectra of β -cyclodextrin (CD) and its bromine-(BrCD) and thioderivatives (TCD). The lower trace represents the SERS spectrum of TCD adsorbed at the surface of a silver SERS substrate (TCD/Ag). Spectra were corrected for broadband background and shifted upward to enhance the clarity of the presentation.



Figure 4. SERS intensity of the C–S stretching band of TCD at 725 cm^{-1} as a function of time during the coating process.

Coating of SERS Substrates with TCD. After being coated with TCD, the substrates show SERS spectra as given in Figure 3. The complete absence of the S-H stretching band in this spectrum confirms the expected chemisorption due to reaction of the thiol groups with the metal surface. Obviously, the major part of the thiol groups reacted with the silver surface, resulting in a multiple attachment of each TCD molecule.

The 498 cm⁻¹ band is located close to a strong unassigned band of CD and its derivatives. Most fingerprint bands are comparatively weak, whereas a strong C–S stretching band appears at 725 cm⁻¹. The appearance of a single C–S stretching band at a position typical for aliphatic thiols in the trans conformation¹⁹ shows that the sulfur groups were attached in a uniform conformation.

The SERS intensity of the C–S stretching band was also analyzed in situ during the coating process to obtain information on the velocity of adsorption (Figure 4). More than 50% of the final intensity was reached within 10 min, and the coating was practically completed after half an hour. The observed curve should represent the relative surface coverage (θ) as a function of time (t), and it could be shown that it fits well with a rate of adsorption proportional to the uncovered portion of the surface $(1 - \theta)$:

$$\theta(t) = \theta_{\max} (1 - e^{-t/T})$$

with a characteristic response time of T = 8.7 min (curve in Figure 4).

Inclusion Complexes at the Surface. The capability of TCDcoated SERS substrates to form inclusion complexes with



Raman Shift (cm⁻¹)

Figure 5. Raman spectra of saturated MO solutions at pH = 7 (a) and pH = 3 (b). SERS spectra of bare silver substrates immersed in saturated MO solution at pH = 7 (c) and pH = 3 (d). SERS spectrum of a TCD-coated substrate immersed in 20 μ M MO solution at pH = 3 (e). Spectra were corrected for broadband background and shifted vertically to enhance the clarity of the presentation.

organic molecules was tested using aqueous solutions of the azo dye methyl orange (MO). Such azo dyes are known to change their structure, thus resulting in marked changes of their vibrational spectra with changing pH and also with complexation with cyclodextrins in aqueous solutions.⁹ Earlier attempts to observe SERS from mixtures of MO and Ag sols failed.^{9,20} Inclusion complexes of MO with 6-(2-mercaptoethylamino)-6-deoxy- β -CD (MEACD), another CD modified by thiol groups, immobilized at colloidal silver were detected by Maedo and Kitano using surface-enhanced resonance Raman scattering (SERRS).⁹

In the work presented here, the adsorption of MO at bare metal substrates immersed in aqueous MO solutions was measurable at the saturation concentration of about 0.61 mM,²¹ whereas practically no SERS bands of MO were detected from a 30-fold diluted (20 μ M) solution. The SERS spectra (Figure 5, spectra c and d) were quite similar to the Raman spectra of dissolved MO (Figure 5, spectra a and b) and changed also considerably with the pH of the solution as the Raman spectra did. Especially, the disappearance of the strong bands of the phenyl–N= stretching vibration at 1143 cm⁻¹ and the N=N stretching vibration at 1446 cm⁻¹ as well as the appearance of the C=C stretching vibration band at 1620 cm^{-1 22} showed the presence of the surface, whereas the azo form is present under neutral conditions in the dissolved and the adsorbed state.

TCD coatings on SERS substrates resulted in distinct changes of the adsorption of MO. First, intense SERS spectra of MO were obtained even for substrates immersed in 20 μ M solutions, where no adsorption was detectable with bare metal substrates. Second, the SERS bands of MO at the coated substrate were characteristic for the azo form at pH = 7 as well as at pH = 3



Figure 6. SERS spectra of toluene (a) and m-xylene (c) adsorbed at TCD-coated substrates. Raman spectra of toluene (b) and m-xylene (d) are given for comparison. Spectra were corrected for broadband background and shifted vertically to enhance the clarity of the presentation.

(Figure 5, spectrum e), thus indicating that no protonation took place under acidic conditions. Third, MO was so strongly adsorbed at TCD-coated surfaces that it was not removable by rinsing with pure water. Rinsing with 10 mM NaCl solutions removed the MO and resulted in substrates that were capable of adsorbing MO again. All these observations proved that there was a strong, but still reversible adsorption of MO with immobilized TCD, preventing protonation of the azo moiety as it is the case for inclusion complexes of MO with CD in solution.⁹ Unlike in the investigation on MEACD-coated substrates allows the exclusion of influences of the metal surface on the protonation behavior and thus provides additional evidence for inclusional complexation at the TCD-coated surfaces.

Adsorption of Gaseous Aromatics. SERS bands of adsorbed aromatic substances were already observed at uncoated substrates at high gas concentrations close to the vapor pressures. At TCD-coated substrates, several of the aromatic compounds could be detected at considerably lower concentrations (Figure 6). Enhanced adsorption at immobilized TCD was observed for benzene, toluene, ethylbenzene, m-xylene, chlorobenzene, and m-dichlorobenzene, whereas o- and p-isomers of xylene and dichlorobenzene were not detectable at these substrates. Retention times at CD-coated gas chromatographic columns did not indicate such a strong stereoselectivity of the adsorption.²³ Therefore, the missing detection of o- and p-isomers may be related to features of the SERS substrates, for example, the presence of silver and sulfur atoms close to the cyclodextrin cavity. The absence of SERS bands of these substances may also be related to a flat orientation of adsorbed molecules and the action of surface selection rules of SERS.²⁴

The SERS spectra of TCD-coated substrates with adsorbed aromatic compounds are apparently a pure superposition of the SERS bands of TCD and bands of the aromatics at practically



Figure 7. Time dependencies of the SERS intensities of the bands of adsorbed *m*-dichlorobenzene at 997 cm⁻¹ (*), *m*-xylene at 999 cm⁻¹ (+), and benzene at 992 cm⁻¹ (×). The intensities were normalized with respect to temporal changes of the intensity of the TCD band at 725 cm⁻¹. The substrates were exposed for 30 min to the following concentrations: 9.8% benzene, 7% *m*-xylene, and 1.4 % *m*-dichlorobenzene. The lines were calculated by fitting exponential decay curves to the adsorption and desorption processes.

the same positions as the Raman bands of the liquid substances.²⁵ Figure 6 shows as an example the SERS spectra of toluene and *m*-xylene, which exhibit the strong, broad TCD band at 725 cm⁻¹ and the bands of toluene at 784 and 1002 cm⁻¹ and of *m*-xylene at 724 and 999 cm⁻¹, respectively. SERS bands of the other substances were observed at the following positions: 992 cm⁻¹ for benzene, 1005 and 1032 cm⁻¹ for ethylbenzene, 1002 and 1022 cm⁻¹ for chlorobenzene, and 998 cm⁻¹ for *m*-dichlorobenzene. The positions of these SERS bands depend clearly on the substituents so that they are suited for an unambigious identification of the adsorbed aromatic compound within the investigated group.

A further advantage of the TCD-coated substrates was that the TCD SERS bands at 498 and 725 cm⁻¹ (Figures 5e and 6) can serve as an internal standard in the evaluation of band intensities of the aromatic adsorbates. By this means, SERS band intensities can be used as a measure for the surface concentration of adsorbates that is independent of the actual SERS enhancement of the respective substrate and the experimental conditions applied.

Time Dependencies of Adsorption. Investigations of the response of SERS intensities from aromatic adsorbates at TCD-coated substrates on concentration changes revealed that only benzene was desorbed completely in a short time (Figure 7), whereas portions of the benzene derivatives remained at the surface for considerable periods after switching to a pure nitrogen atmosphere (see Figure 7 for *m*-xylene and *m*-dichlorobenzene). Owing to this slow desorption, the SERS intensities were not a pure measure of the present gas concentration. However, the slow desorption may be useful for accumulative detection purposes as required, for instance, in exposure measurements or the detection of slowly changing low concentrations.

 TABLE 2: Limits of Detection of Gaseous Aromatic

 Substances at TCD-Coated SERS Substrates after Exposure

 Times of 10 min (* after 24 h Exposure)

substance	limit of detection (ppm)
benzene	10 000
<i>m</i> -xylene	1400
toluene	400
chlorobenzene	250
<i>m</i> -dichlorobenzene	15*
o- and p-dichlorobenzene	not detected
o- and p-xylene	not detected

Analyses of time dependencies at different concentrations showed that fast and slowly desorbing adsorbate portions can be observed at higher concentrations of the derivatives (Figure 7, m-xylene), whereas at lower concentrations the slowly desorbing adsorbate dominates (Figure 7, m-dichlorobenzene). Benzene and the fast desorbing adsorbates formed at higher concentrations of the derivatives adsorbed and desorbed with response times below 2 min. The response times of the slowly desorbing adsorbate portion were determined by exponential fits for m-dichlorobenzene to be 6.5 min for the adsorption at a concentration of 1.4% and about 2 h for the desorption in the initial period. Later, the response time increased further and reached about 30 h after a few days. Maybe the response in the initial period was superposed by residuals of a faster desorbing portion of the adsorbate. The large ratio of the velocities of adsorption and desorption at the investigated concentration promises that clearly lower gas concentrations may be applicable without decreasing the surface coverage clearly.

At gas concentrations close to the vapor pressures, very similar SERS intensities were observed for the fast and the slowly desorbing adsorbate portions of the benzene derivatives. This points to similar numbers of the two different adsorption sites, as would be the case with the adsorption of two aromatic molecules per TCD cavity. One molecule may be strongly adsorbed deep inside the cavity by interactions including one or both substituents. Adsorption and desorption at this site may also be slowed by an activation barrier at the opening of the cavity. The second molecule of the derivatives and all benzene molecules were weakly adsorbed, as indicated by the high equilibrium gas concentrations and without a high barrier as perceptible from the fast response. These weakly adsorbed portions may be located closer to the rim of the cavity, at unfavorable adsorption sites left after adsorption of a first molecule, or they may not interact efficiently with the TCD cavity because of missing substituents. However, a detailed analysis of the adsorption sites and their interactions with the aromatic molecules was not possible on the basis of the present SERS data.

It should be noted that a fast desorption of the strongly adsorbed portions was achieved by rinsing the substrates with water. After drying, these substrates were again capable of adsorbing aromatic compounds.

Limits of Detection. The limits of detection for gaseous aromatic compounds were determined by measuring SERS spectra after an exposure to the respective concentration for 10 min (Table 2). As expected from the absence of a strongly adsorbed portion, benzene showed a clearly higher limit of detection than the other compounds. Benzene derivatives were detectable at concentrations of several 100 ppm with a distinct effect of the substituents on the limits of detection.

Even lower limits of detection can be reached for substances forming slowly desorbing adsorbates at the surface by the application of longer exposure times. This was demonstrated





Figure 8. Concentration dependencies of the SERS intensities of the bands of adsorbed benzene at 992 cm⁻¹ (\blacksquare), chlorobenzene at 1002 cm⁻¹ (\blacksquare), and *m*-dichlorobenzene at 997 cm⁻¹ (\blacktriangle). The intensities were normalized with respect to temporal changes of the intensity of the TCD band at 725 cm⁻¹. The lines were calculated by fitting a linear function to the benzene data and exponential decay curves to the data of the derivatives.

with *m*-dichlorobenzene, for which 15 ppm were detectable after 24 h of exposure (Table 2).

Concentration Dependencies. In principle, determinations of gas concentration or exposure should be possible on the basis of SERS intensities in equilibrium and measurements as a function of time. The quantitative evaluation of these measurements requires calibration curves, which may be obscured by the presence of two adsorbate portions with different temporal response and affinity to the surface.

The concentration curves shown in Figure 8 were taken after successive application of pure nitrogen and stepwise increasing concentrations of the respective substances for 5 min in each case. The strongly adsorbed substituted aromatics were not completely desorbed during the intermediate flushing with nitrogen, but this procedure was the only possibility of obtaining concentration curves in a reasonable time.

The curve for benzene increases linearly up to comparatively high concentrations, whereas the other curves show clear saturation effects already at low concentrations. These differences appearently correlate with the presence of the strongly adsorbed portion. The weakly adsorbed benzene cannot saturate the surface even at the highest concentrations applied. The strongly adsorbed species of the chlorosubstituted aromatics seem to cover a considerable portion of the TCD cavities already after admission of comparatively low concentrations.

Polycyclic Aromatic Hydrocarbons (PAHs). PAHs are rather hazardous compounds, even at very small concentrations. Attempts to adsorb traces of PAHs from solution or the gas phase at metal substrates and to detect them by SERS failed, probably owing to the absence of groups attaching to the metal surface. PAHs in methanol were detectable after evaporation of the solvent on a SERS substrate.²⁶



Figure 9. SERS spectrum of naphthalene at a TCD-coated substrate (a). The Raman spectrum of solid naphthalene (b) is given for comparison.

The size of the TCD cavity seemed to be sufficient for the inclusion of some of the smallest PAH molecules. Therefore, first experiments for the detection of gaseous PAHs at TCD-coated SERS substrates were made with naphthalene and anthracene containing two and three aromatic rings, respectively. Clear SERS bands of naphthalene were observed at TCD-coated substrates after storing them for 30 min in a nitrogen atmosphere above solid naphthalene (Figure 9), where a concentration around 100 ppm should be present according to the vapor pressure of the substance. Owing to the appearance of all strong naphthalene Raman bands at practically the same positions in the SERS spectrum, a reliable identification of the substance was possible. The signal-to-noise ratio of the two strongest bands suggests that even lower concentrations should be detectable.

Anthracene could not be detected in the atmosphere above the solid substance, even after overnight storage. This might be related to gas concentrations of the substance in the low ppb range owing to a vapor pressure being about 4 orders of magnitude smaller than that of naphthalene. Substrates previously stored above anthracene were no more capable of a subsequent adsorption of naphthalene, whereas this capability was recovered by rinsing with water and drying. The latter observation points to a coverage with anthracene that did not result in detectable SERS intensities. Possibly, these larger molecules could not be properly included in the TCD cavities and were, therefore, adsorbed at a larger distance from the metal surface, where the enhancement factors can be clearly lower.

Aromatic Compounds in Water. Finally, it should be mentioned that most investigated aromatic compounds were not detectable at SERS substrates immersed in their aqueous solutions. *m*-Dichlorobenzene was the only substance that was slowly adsorbed and detected at a concentration of 0.4 mM.

Cyclodextrins are known to form inclusion complexes with highly concentrated aromatics in water.²⁷ An investigation of the retention of various compounds at cyclodextrin-coated columns for gas chromatography showed that water vapor affects the inclusional complexation strongly.²³ Therefore, it has to be assumed that competitive adsorption of water prevents the adsorption of most aromatic compounds at low concentrations. This effect may be useful in the detection of gaseous aromatics, since it reduces not only the surface coverages but also accelerates the desorption as was shown in the earlier investigation.²³ Maybe a simultaneous or intermediate admission of water vapor in defined concentrations would allow control of sensitivity and response time of TCD-coated chemical SERS sensors or regeneration of them quickly.

Conclusions

TCD has been prepared from CD and chemisorbed at silver SERS substrates by the reaction of its thiol functions with the metal surface. The capability of surface-bound TCD to form inclusion complexes has been proven by the adsorption of MO and the stability of its azo form at the surface at low pH. The TCD-coated substrates have been used for the detection and identification of low concentrated aromatics in the gas phase. Most detected aromatics have formed two differently adsorbed adsorbate portions. The stronger adsorbed portion has made the detection of concentrations in the ppm range possible but with comparatively large response times. Experiments with naphthalene have shown that this polycyclic aromatic compound can also be adsorbed at TCD-coated surfaces.

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