

Surface plasmon enhanced Raman spectroscopy with HS(CH₂)₂₁OH on different metals

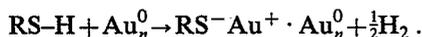
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A method is presented that expands plasmon surface polariton field enhanced Raman spectroscopy (PSPR) to arbitrary metal substrates. Using this technique the ratio of the Raman tensor elements α_{zz}/α_{xx} for the alkane chain in HS(CH₂)₂₁OH on silver is determined. Based on this knowledge we also investigate PSPR spectra of HS(CH₂)₂₁OH adsorbed on copper and gold in order to determine its tilt angle with respect to the metal surface.

I. INTRODUCTION

The growing interest in mono- and multilayer assemblies¹⁻³ originates from their potential use as ultrathin coatings with special and purposefully designed properties in as different fields as electronic device fabrication, biological sensors, etc.² Promising candidates are thiol compounds which build monolayers by the self-assembly technique (SAM).^{3,4} Chemisorption of alkanethiols on gold gives the Au(I) thiolates (RS⁻) species probably by



While the mechanism involved in the reaction of alkanethiols with gold(0) is not completely understood, it has been recently shown both electrochemically¹⁷ and using Raman spectroscopy,¹⁸ that the species chemisorbed on the gold surface is indeed a thiolate. However, the exact nature of the bonding between the thiolate sulfur and the gold or silver lattice has never fully been understood. Strong and Whitesides studied monolayers of docosanethiol [CH₃(CH₂)₂₁SH] on single-crystal foils with an exposed (111) surface using electron diffraction.¹⁹ They found that the symmetry of sulfur atoms in a monolayer of docosanethiol on the Au(111) surface is hexagonal with an S··S spacing of 4.97 Å, and calculated area per molecule of 21.4 Å². Later, after helium diffraction studies,²⁰ and a re-evaluation of the electron diffraction data,²¹ it was confirmed that the structure formed by docosanethiol on Au(111) is commensurate with the underlying gold lattice and most likely is a simple ($\sqrt{3} \times \sqrt{3}$)R30° overlayer. Thus the S··S spacing corresponds to the second-nearest-neighbor distance on Au(111). Very recent scanning tunneling microscopy (STM) studies confirm this conclusion.²² LEED-Auger studies of CH₃S on Ag(111),^{23,24} suggest an S··S distance of 4.41 Å [epitaxial structure of ($\sqrt{7} \times \sqrt{7}$)R10.9°]. The most detailed experiments to date were carried out on monolayers adsorbed on (111) surfaces. SAMs of alkanethiolates on Au(111) and Ag(111)

surfaces are very different. Thus while there has been a consensus on the structure of thiols on Au(111), the experimental picture for thiolates on Ag(111) has been considerably less clear. The tilt angle of alkyl chains in their assembly on Au(111) is ~30°. This consistent value has been observed by many groups, for many different thiolates, and using different analytical techniques (e.g., FTIR,²⁵ electron diffraction,¹⁹ x-ray diffraction,²⁶ etc.) On the other hand, Porter, using our published FTIR spectrum of a SAM of octadecanethiolate (SC₁₈H₃₇, ODT) on Ag(111)²⁷ calculated a tilt angle of ~7°. In another case, we found that the FTIR spectrum of HUT/Ag(111) [HUT being HO(CH₂)₁₁SH] is featureless, indicating that the chains in this monolayer are perpendicular to the surface.²⁹ In a detailed study comparing thiols on gold, silver, and copper, Laibnis *et al.* reported that the tilt angle in monolayers on silver is 12°. Walczak *et al.* reported a tilt angle of 13°, and very recent Raman studies suggested a tilt angle of 15°. This is quite a range of tilt angles, indicating that there may be a correlation between surface details, preparation protocol, and the monolayer structure. Indeed, Fenter *et al.* carried out x-ray studies of thiols on gold and on the most carefully prepared sample of Ag(111) to date.²⁶ Their most current data shows unambiguously that the tilt angle in thiols on silver may be as small as 3° ± 1°.³²

In a previous work we showed that propagating PSP modes on silver coated gratings can be used to observe Raman spectra of thin Langmuir-Blodgett-Kuhn (LBK) multilayers.⁶ We could demonstrate that the involved field-enhancement mechanisms allow for the recording of Raman spectra of even ultrathin organic layers and that the well-defined field polarization of the PSP modes (calculated on the basis of Maxwell's theory) allow for a quantitative analysis of Raman data, e.g., in terms of a tilt angle of rodlike molecules relative to the substrate normal. The present study is a continuation of this work by applying this technique to self-assembly monolayers of HS(CH₂)₂₁OH, again analyzing the spectral region of the CH₂ stretching vibrations. Based on the above mentioned thorough studies of alkanethiols on silver we assume in a first step HS(CH₂)₂₁OH standing almost perpendicular on silver in order to determine the ratio of the unknown Ra-

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man scattering tensors α_{zz}/α_{xx} . Based on this knowledge we continue our investigations now looking for the tilt angle of HS(CH₂)₂₁OH on gold and copper substrates.

II. THEORY

The analysis of the experiments is based on the theoretical treatment given in the literature.⁵⁻¹⁰ For a thorough treatment of surface plasmons we refer the reader to a monograph by Raether.⁷ However, a summary of important theoretical aspects is given in the subsequent paragraphs including a refinement which allows to calculate the PSP polarization within a thin film sandwiched between two semi infinite half spaces [cf. (i)].

(i) For the quantitative description of PSP propagation in the X direction at a flat interface in the XY plane separating two semi-infinite spaces of a metal (with dielectric constant ϵ_m , e.g., silver) and a dielectric (with dielectric constant ϵ_d , e.g., air) at $Z=0$, one can derive the polarization of the evanescent electric field with components E_{zd} and E_{xd} in the dielectric, where k_{xd}^{PSP} and k_{zd}^{PSP} $= \sqrt{\epsilon_d(\omega/c)^2 - k_{xd}^{\text{PSP}2}}$ represent the components of the PSP wave vector in the dielectric⁷

$$\frac{|E_{zd}|^2}{|E_{xd}|^2} = \frac{|k_{xd}^{\text{PSP}}|^2}{|k_{zd}^{\text{PSP}}|^2} = \frac{|\epsilon_m|}{|\epsilon_d|}. \quad (1)$$

Since ϵ_m strongly depends on the frequency (with ϵ_d being almost constant in the considered wavelength range) the polarized field probing the Raman scattering tensor, e.g., of our thiol, is wavelength dependent too. At this point we refine Eq. (1) since it is only applicable at boundaries between two semi-infinite media. To adapt Eq. (1) to an air/thiol monolayer/metal system we have to consider the continuity of the tangential component of the electric field (E_x) and the normal component of the electric displacement ($D_z = \epsilon E_z$) at the air/thiol interface. With Eq. (1) the polarization in the thiol monolayer becomes (T refers to the thiol monolayer)

$$\begin{aligned} \frac{|E_{zT}|}{|E_{xT}|} &= \frac{|E_{z\text{air}}|}{|E_{x\text{air}}|} \frac{|\epsilon_{\text{air}}|}{|\epsilon_T|} \\ &\stackrel{(1)}{=} \frac{|k_{x\text{air}}^{\text{PSP}}|}{|k_{z\text{air}}^{\text{PSP}}|} \frac{|\epsilon_{\text{air}}|}{|\epsilon_T|} \\ &= \frac{|k_{x\text{air}}^{\text{PSP}}|}{\sqrt{\epsilon_d(\omega/c)^2 - k_{x\text{air}}^{\text{PSP}2}}} \frac{|\epsilon_{\text{air}}|}{|\epsilon_T|}, \end{aligned} \quad (2)$$

where $k_{x\text{air}}^{\text{PSP}}$ is obtained from a numerical calculation of the PSP dispersion relation (cf. Fig. 2) which is based on a matrix formalism taking into account interferences between air-monolayer and monolayer-metal surface polaritons.¹³

(ii) The dependence of the PSP Raman scattering intensity on the employed laser wavelength can be described according to Ref. 9 as

$$\begin{aligned} I_R = & \left| \frac{E_{z\text{in}}E_{z\text{out}}}{E_{x\text{in}}E_{x\text{out}}} a_{zz} + j \left[\frac{E_{z\text{in}}}{E_{x\text{in}}} (a_{xz} \cos \Theta + a_{yz} \sin \Theta) \right. \right. \\ & \left. \left. + \frac{E_{z\text{out}}}{E_{x\text{out}}} a_{zx} \right] - (a_{xx} \cos \Theta + a_{yx} \sin \Theta) \right|^2, \end{aligned} \quad (3)$$

where in contrast to Refs. 5-10 we take the ratio E_z/E_x inside the thiol monolayer using Eq. (2) at the excitation (in) and emission (out) wavelength, respectively, a_{ij} are the Raman tensor elements in a *space fixed* coordinate system and Θ is the tilt angle of the rodlike alkane chain of the thiol with respect to the surface normal of the substrate.

(iii) The a_{ij} can be calculated for all *trans* configured infinitely long molecules on the basis of group theoretical considerations.¹⁰ The symmetric and asymmetric CH₂ vibrations correspond to $A_g(\alpha_{xx}, \alpha_{yy}, \alpha_{zz})$ and $B_{1g}(\alpha_{xy})$ species, respectively. (α_{ij} are the Raman tensor elements in the *molecular fixed* coordinate system.)

(iv) From waveguide Raman spectroscopy of cadmium arachidate (CdA) multilayer assemblies it was deduced that for CH₂ molecules the Raman tensor elements $\alpha_{xx}^2 = \alpha_{yy}^2$ and $\alpha_{xy}^2 = 2.5 \alpha_{xx}^2$.¹¹ Due to the similarity of CdA (Cd²⁺[COO⁻(CH₂)₁₈CH₃]₂) and alkane thiols HS(CH₂)_nR these findings are assumed to be also valid for thiols. Since we are only interested in the orientation of alkane chains with respect to the substrate we can use azimuthally averaged molecular polarizabilities. Thus our only unknown parameters reduce to the tilt angle Θ and the ratio α_{zz}/α_{xx} .⁵

III. EXPERIMENT

Since details of our experimental set up (Ar⁺ Laser, Spex 1877 Triplemate Spectrometer) and PSPR using grating coupling are described elsewhere^{5,6,12} we just give a brief summary: polarized surface plasmons are resonantly enhanced with laser light of energy $h\nu_L$ using a grating coupler at a well defined angle Θ_{in} . Now, by an inelastic Raman scattering process, an energetically lower PSP state, Stokes shifted by $\Delta\nu$, is generated. This couples out at a well defined scattering angle Θ_{out} .

In a first step we measure HS(CH₂)₂₁OH—which is assumed to stand almost perpendicular on silver—on a silver coated grating at different excitation wavelengths in order to determine the ratio of the Raman scattering tensors α_{zz}/α_{xx} . The thiol is adsorbed for ca. 3 h immediately after evaporation of 150 nm silver with 0.5 nm/s on a glass substrate with an ion etched grating (grating constant 390 nm, modulation height $h=15$ nm).¹² The incident laser power on the sample varies between 10-80 mW with integration times of 10-40 min.

IV. RESULTS AND DISCUSSION

We focus in this paper on the asymmetric and symmetric CH₂ vibrations at ~ 2850 and ~ 2890 cm⁻¹, respectively. The wavelength dependent spectra of the thiol are

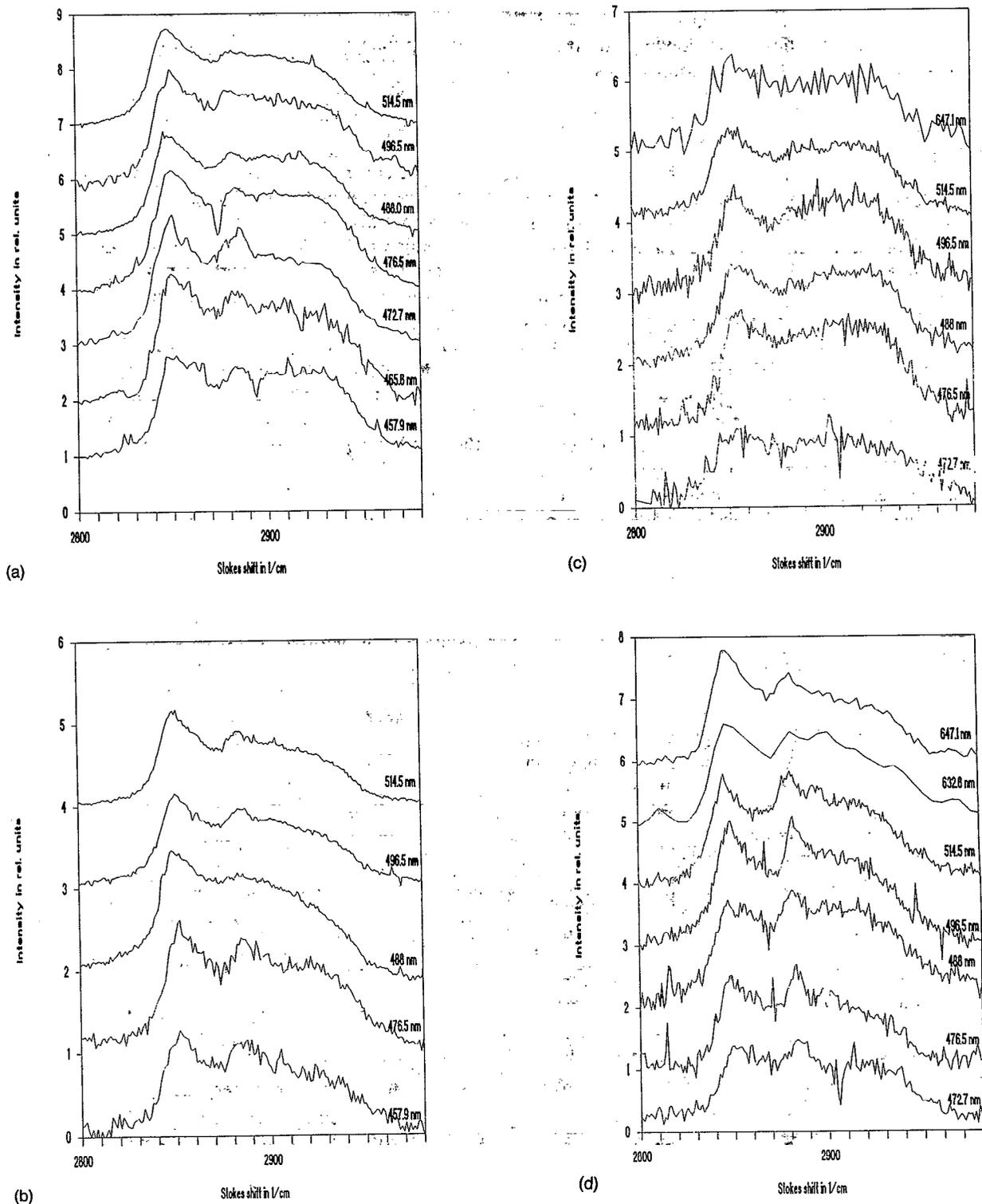


FIG. 1. Wavelength dependent Raman spectra between 2800 and 3000 cm^{-1} for HS(CH₂)₂₁OH: (a) on silver, (b) on silver sandwich substrates (cf. Fig. 4), (c) on copper sandwich substrates (cf. Fig. 4), (d) on gold sandwich substrates (cf. Fig. 4).

depicted in Fig. 1(a). We define the ratio of the Raman peak intensities at 2880 and at 2850 cm^{-1} as⁸

$$\nu(\lambda) = \frac{I_R(2880 \text{ cm}^{-1})}{I_R(2850 \text{ cm}^{-1})} \quad (4)$$

Using a numerically calculated dispersion curve for PSPs on silver gratings, [Fig. 2(a)]¹³ we calculated according to Eq. (2) the polarization of PSPs in the thiol monolayer [$\epsilon_T = 2.1025$ Ref. (3)]. From our own ellipsometrical

and PSP-spectroscopical measurements we determined the thickness of the thiol layer to $30.6 \pm 2 \text{ \AA}$ on silver with the assumption that $\epsilon_T = 2.1025$. Compared to the theoretically expected thickness which amounts to 31 \AA (Ref. 14)

and to the findings from different authors (cf. Sec. I) which indicate that long chain thiols are densely packed in a crystallinelike structure with an almost perpendicular orientation of the alkane chain on silver we also assumed

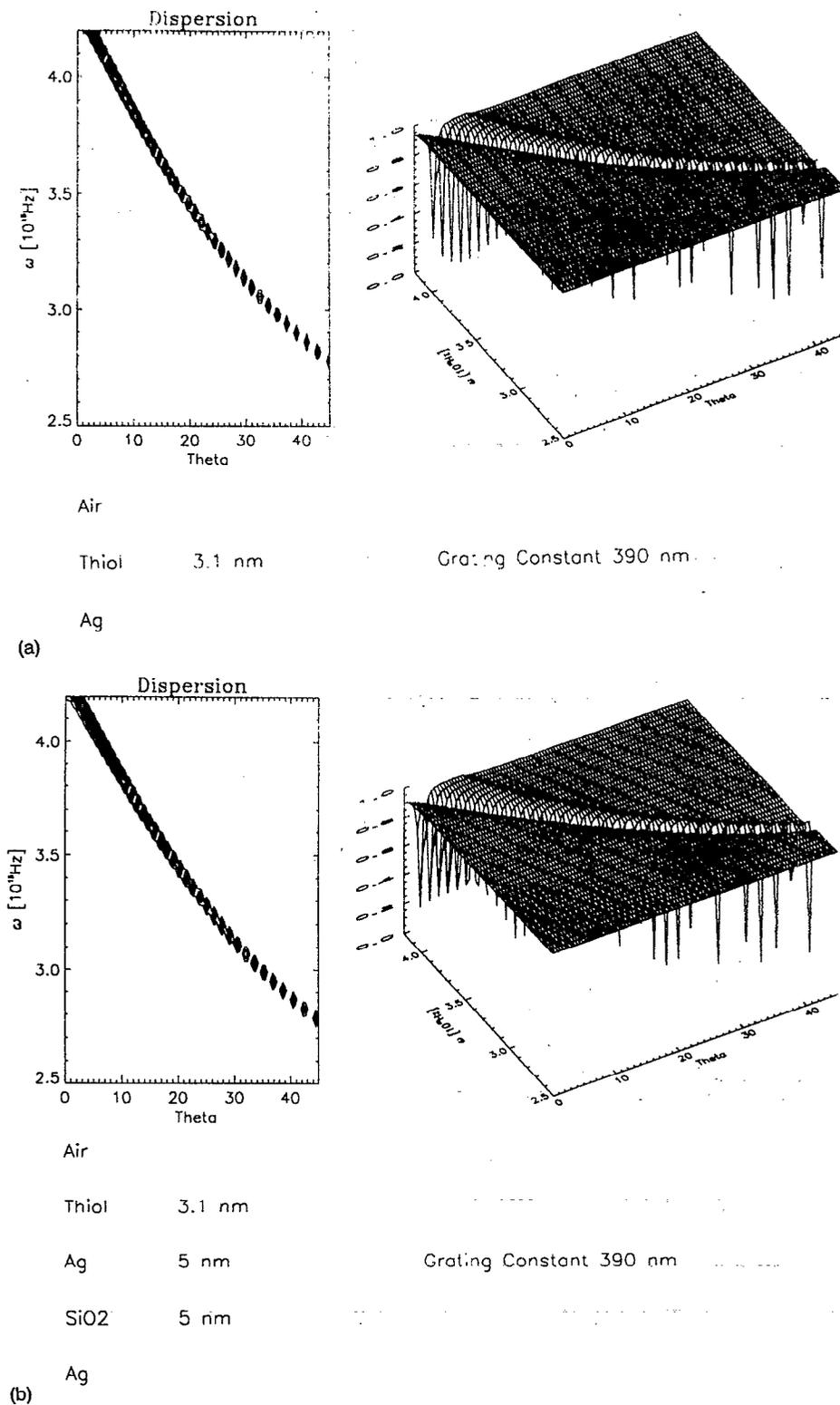


FIG. 2. Calculated dispersion relation for grating coupled PSPs. The dispersion relation yields $k_{\text{air}}^{\text{PSP}} = \omega/c \sin \Theta$ to calculate the polarization according to Eq. (2). Right-hand side: from grating under angle Θ reflected intensity of p -polarized light of frequency ω . Left-hand side: from right-hand side resulting dispersion curve for PSPs. (a) On a silver/thiol/air system. On a silver/5 nm SiO_2 /5 nm S3/thiol/air system (cf. Fig. 4): (b) S3=Ag, (c) S3=Cu, (d) S3=Au.

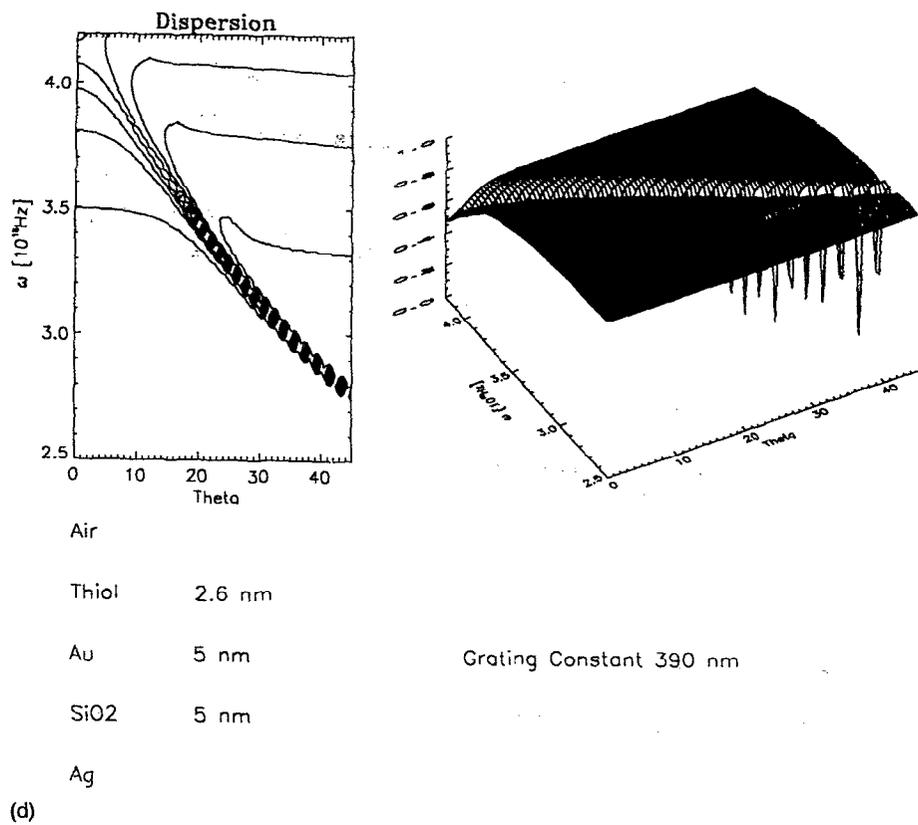
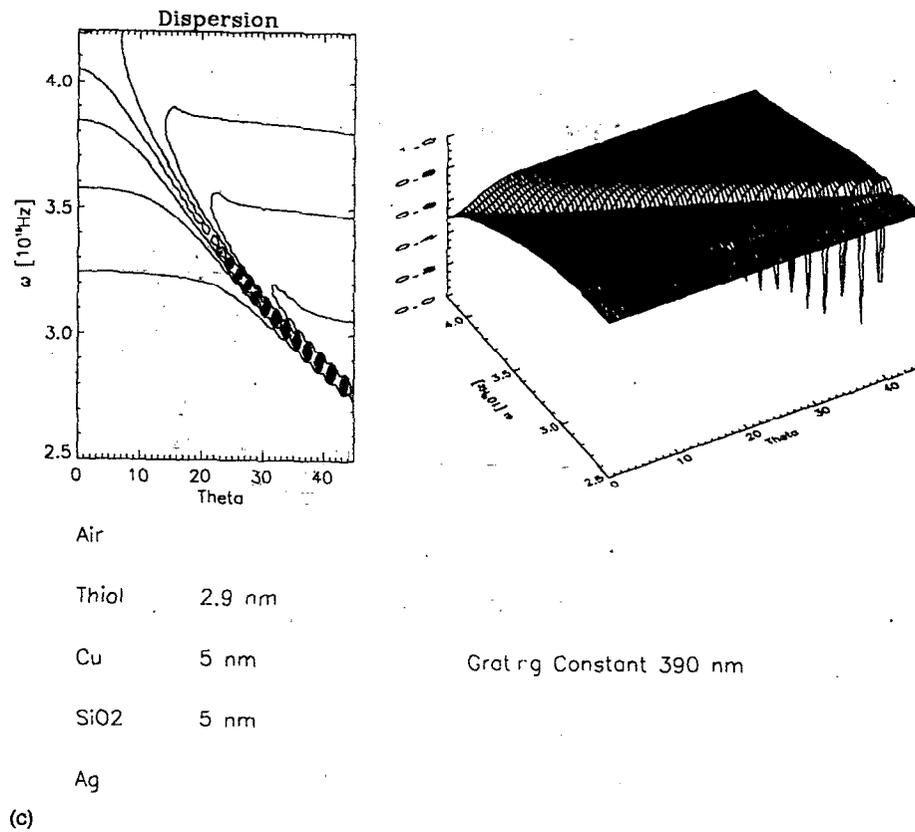


FIG. 2. (Continued.)

that the chains are oriented almost normal to the silver (i.e., tilt angle $\Theta \approx 5^\circ$). Based on this assumption, we start the analysis of the PSPR spectra aiming for the determination of the ratio α_{zz}/α_{xx} .

Figure 3(a) shows the $\nu(\lambda)$ values obtained from Fig. 1(a). The full lines show the expected theoretical $\nu(\lambda)$

values calculated with Eqs. (2), (3), and (4) using the dispersion relation from Fig. 2(a) for different ratios of the unknown parameter α_{zz}/α_{xx} . In a first approximation—to show the course of $\nu(\lambda)$ with different ratios α_{zz}/α_{xx} —we assume a tilt of $\Theta = 0^\circ$ [Fig. 3(a₁)]. Owing to different publications (cf. Sec. I) which indicate an almost perpen-

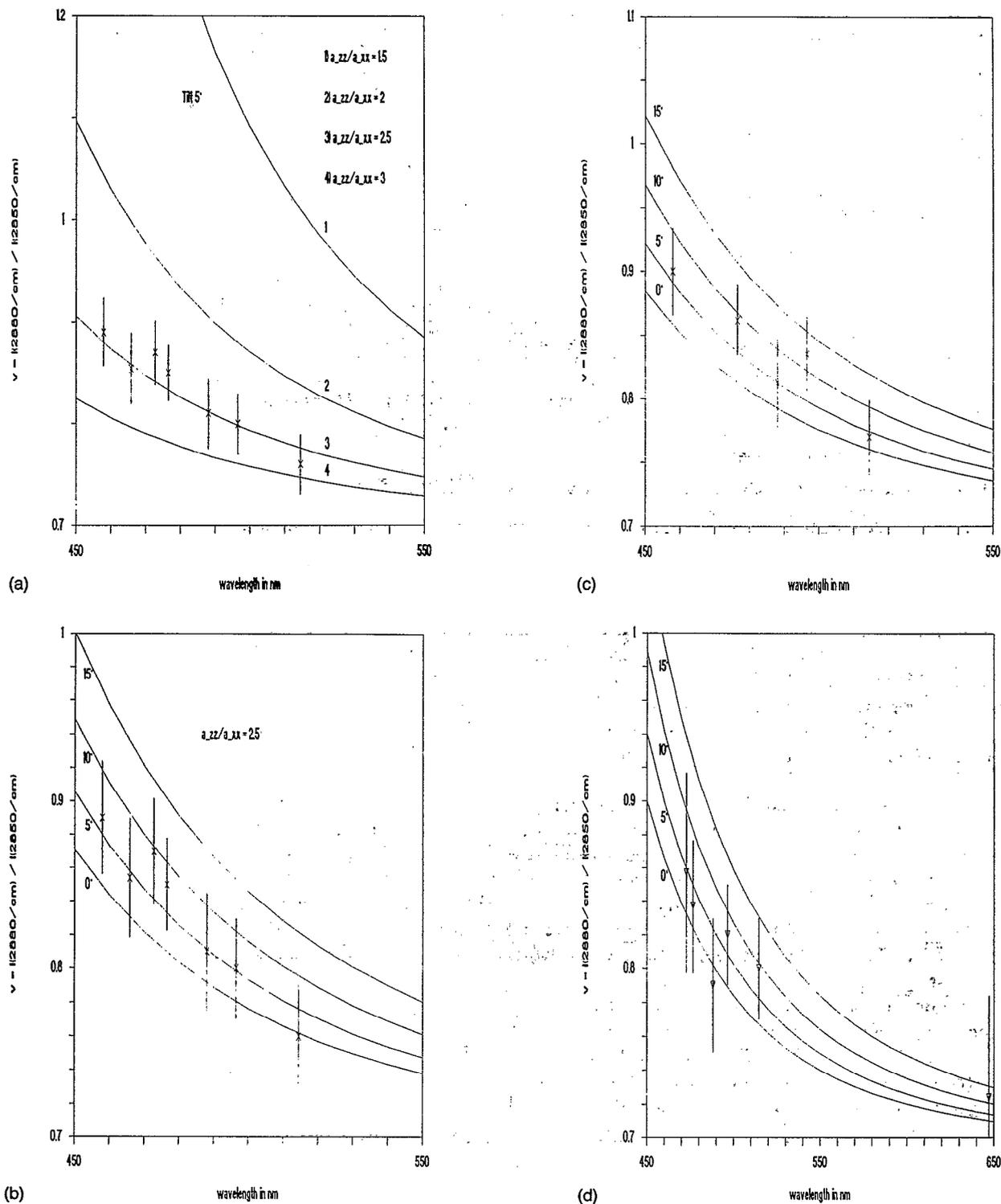
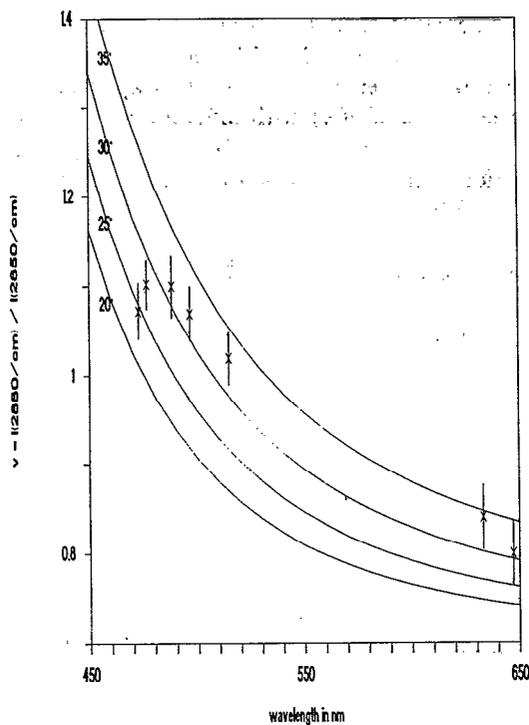


FIG. 3. (a)–(e) Comparison between experimentally obtained $\nu(\lambda)$ values and theoretically calculated curves using data from Figs. 1(a)–1(d), respectively.



(e)

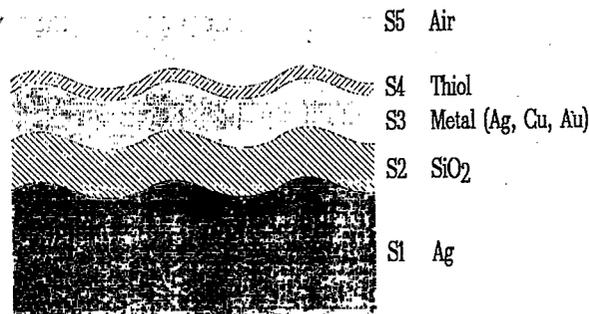
FIG. 3. (Continued.)

dicular tilt of thiols on silver we assume a tilt of $\Theta = 5^\circ \pm 5^\circ$ and present in Fig. 3(a₂) that the best agreement between theory and experiment is found for the ratio $\alpha_{zz}/\alpha_{xx} = 2.5$. Due to the error in the Raman spectra [cf. Fig. 1(a)] this ratio has an uncertainty of ± 0.25 .

After the determination of this essential parameter α_{zz}/α_{xx} a method is presented that expands PSP enhanced Raman spectroscopy to arbitrary metal substrates. Using this technique a quantification of tilt angles based on PSPR spectra of HS(CH₂)₂₁OH adsorbed on copper and gold is discussed.

Since it is well established that thiols HS(CH₂)_nR adsorb having different tilt angle of their alkane chains with respect to the substrate HS(CH₂)₂₁OH is a good candidate for our PSPR studies on silver, gold and copper. Unfortunately, there is no amplification of PSPs in the spectral region between 450–520 nm on Au and Cu.¹⁵ Even for longer wavelengths the amplification for the Au and Cu is manifold smaller than that of silver due to interband transitions leading to strong absorptions. To overcome this problem we developed a preparation technique for PSPR substrates. Preserving the large PSP amplification on silver and at the same time retaining the special adsorption characteristics of thiols on Au and Cu we evaporated so-called *sandwich substrates* (Fig. 4).

Gratings were coated with 150 nm silver at 0.5 nm/s and subsequently with a 5 nm thick SiO₂ layer at rates between 0.05–0.1 nm/s. On top of the silicon oxide we evaporated S3=Ag/or Au/or Cu with $d_{s3} = 5$ nm at 0.05–0.1 nm/s. Following the evaporation process the samples were immediately immersed in a freshly prepared thiol so-

FIG. 4. Structure of *sandwich* substrates for PSPR on different metals S3.

lution for adsorption. However, due to the strong reaction of copper with oxygen the presence of a layer of copper oxide can never be ruled out. After at least 3 h of adsorption the substrates were taken from the solution and rinsed with ethanol. As before, the adsorbed thiol was monitored ellipsometrically to check that its thickness corresponds to the thiol adsorption on the, respectively, taken metal S3. A comparison between our ellipsometrically measured thicknesses and the theoretically calculated length of a HS(CH₂)₂₁OH molecule gives rise to a tilt of the alkane chain of $\sim 16^\circ$ and $\sim 31^\circ$ on copper and gold, respectively. The ellipsometrical measurement turned out to be quite essential since it happened from time to time that thiols adsorbed on S3=Au showed typical thicknesses of thiols adsorbed on silver if we omitted the insulating SiO₂ layer between S1 and S3. This was attributed to an interdiffusion process between S1 and S3. However, these complications were completely avoided by the additional insulating SiO₂ layer which acts as a diffusion barrier between S1 and S3.

Since the numerically calculated PSP dispersion curves for the systems Ag/thiol/air [Fig. 2(a)] and the here used Ag/SiO₂/Ag/thiol/air system [Fig. 2(b)] show no significant differences up to 450 nm ($= 4.19 \times 10^{15}$ Hz) we tried to verify our previous findings for $\alpha_{zz}/\alpha_{xx} = 2.5$. In doing so we had to compare the experimentally obtained ratio $\nu(\lambda)$ of the symmetric and asymmetric CH₂ vibration [Fig. 1(b)] with the calculated ratios using Eqs. (2)–(4). As before [cf. Fig. 3(a₂)] we assumed $\alpha_{zz}/\alpha_{xx} = 2.5$ and Θ as fitting parameter. The best agreement between theory and experiment was again found for $\alpha_{zz}/\alpha_{xx} = 2.5$ and $\Theta = 5^\circ \pm 5^\circ$. Based on this verification we continued our comparison for S3=Cu and Au. Although the PSP damping in Cu and Au between 450 and 520 nm using *sandwich* substrates is greatly reduced, there still exists a substantial PSP damping for $\lambda < 470$ nm. This can be seen both from the increasing width of the theoretically calculated PSP dispersion in Figs. 2(c) and 2(d) and from the reduced quality of the corresponding Raman spectra at 472.7 nm in Figs. 1(c) and 1(d). To get additional data points we took PSPR spectra with a He–Ne and Kr⁺ laser at 632.8 and 647.5 nm, respectively. The spectra of HS(CH₂)₂₁OH on *sandwich* substrates with S3=Cu and Au are shown in Figs. 1(c) and 1(d). Their consistency with theory was again checked using the aforementioned ratio $\alpha_{zz}/\alpha_{xx} = 2.5$ and a variable tilt angle Θ for the alkane chain [Figs. 4(c) and

4(d)]. The comparison between theory and experiment yields the following tilt angles for HS(CH₂)₂₁OH on different substrates

$$\Theta_{\text{Ag}} = 5^\circ \pm 5^\circ,$$

$$\Theta_{\text{Cu}} = 5^\circ \pm 5^\circ,$$

$$\Theta_{\text{Au}} = 30^\circ \pm 5^\circ.$$

The tilt angles are in good agreement with values obtained by different authors with substantially different methods as grazing incidence FTIR, ellipsometry, PSP spectroscopy.

V. CONCLUSION

We showed that (i) for alkane chains the best ratio for α_{zz}/α_{xx} is 2.5 ± 0.25 ; (ii) the preparation of Ag/SiO₂/metal/film substrates expands PSPR to virtually arbitrary substrates; (iii) using sandwich substrates it is possible to calculate orientations of molecules, e.g., the tilt angles of HS(CH₂)₂₁OH on Cu, Au with $\Theta_{\text{Cu}} = 5^\circ \pm 5^\circ$, $\Theta_{\text{Au}} = 30^\circ \pm 5^\circ$.

We conclude that PSPR is a powerful tool for the determination of tilt angles of monolayers adsorbed on different substrates. Especially if one is interested in finding small deviations of the alkane chain from the surface normal. This is evident by a comparison to a complementary method: Using grazing incidence FTIR¹⁶ the difference in intensity of a dipole moment oscillating normal to the surface and the same dipole moment tilted by 15° is

$$\Delta I = \frac{\cos 15^\circ}{\cos 0^\circ} = 0.97,$$

whereas PSPR on silver yields

$$\Delta I = \frac{\nu(460 \text{ nm}, 0^\circ)}{\nu(460 \text{ nm}, 15^\circ)} = 0.87.$$

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- ³²Tilt angles varied from 3° to 8° ± 1°.