Deriving the complete molecular conformation of self-assembled alkanethiol molecules from sum-frequency generation vibrational spectra

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The sum frequency generation (SFG) spectrum of CH_2 and CH_3 modes in the self-assembled monolayer of octadecanethiol is modeled in order to understand the reasons of the very low SFG intensity of CH_2 modes and to investigate quantitatively the two types of L-shaped conformations qualitatively suggested in the literature. CH_2 modes are assumed local in order to calculate easily the spectrum of any conformation, and *ab initio* molecular hyperpolarizabilities are used. It is found that the absence of CH_2 bands does not imply an all-trans conformation and *vice versa*. Several conformations are compatible with SFG, but only one of them can be arranged on Au(111) and completely agrees with x-ray diffraction. All conformational details of the L-shape molecules are obtained.

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I. INTRODUCTION

Self-assembled molecules (SAMs) are widely used for many technological applications such as biosensors or molecular electronics.[1] The assembled molecules are often constituted of an alkyl chain anchored by a thiolate bond to a Au substrate and terminated by a functional group for photonic, chemical, or biological purpose. A quasisolid molecular layer is obtained spontaneously, where the alkyl chains are stretched with an all-trans conformation along most of the chain. This occurs in a time scale of a few hours. The process of self assembly is relatively easy in the case of the prototype alcanethiols but it can be difficult and may fail when large or reactive terminal groups are used. Interactions between the two ends of the molecules or between the functional group and the substrate, or steric hindrance, may prevent the alkyl chains to stretch. Therefore a more detailed knowledge of the conformation of the chains might allow improvement of the self-assembly process.

SAMs are studied with many experimental techniques, including optical linear and nonlinear probes, electron and local probe microscopies, and x-ray and He atom diffractions.[1,2] These techniques characterize best the molecule-substrate bonding and the arrangement of the terminal group on the air side. Conclusions concerning the molecular conformation in between remain difficult to draw due to the floppy and multidimensional nature of the alkyl chains which often constitute part of the molecule. Ellipsometry allows estimation of the SAM height. Infrared reflection absorption spectroscopy (IRAS) compares bulk and SAM spectra and derives average orientational parameters of the alkyl chain. IRAS and sum frequency generation (SFG) provide the orientation of the SAM functional group.[3] In this work we show that SFG can be more informative and can provide the whole molecular conformation in favorable cases such as alkanethiols.

So far, the observed very weak intensity of the methylene stretching modes in the SFG spectra of alkanethiols has been explained by local inversion symmetry centers in the energetically preferred all-trans conformation.[4] The appearance of methylene modes are in general attributed to conformational defects. Typically, the methylene modes are observed by SFG at the early stages of self-assembly[5] or when large functional groups attached to the alkyl chain make the all-trans conformation less favorable due to steric hindrance.[6] This interpretation of the centrosymmetry of the alkyl chain is however not strictly correct because the molecule is not exactly centrosymmetric. Considering that the CH_2 modes are not interacting strongly,[7] a local mode description can be used. Within this approximation, the contributions to the SFG spectrum of CH_2 groups related by local centrosymmetry cancel. For an odd number of CH_2 groups, the SFG spectrum must contain a contribution from the unpaired CH_2 group and carry information on its orientation. Providing that the orientations of CH_3 and all CH_2 groups are related in a geometrical description of the whole molecule, more information might be extracted from SFG spectra by modeling the CH_3 and CH_2 bands together.

A series of experiments on SAMs of alkanethiols using x-ray diffraction,[8–10] He atom scattering,[11] SFG,[12] scanning tunnel microscope (STM),[13,14] and high-resolution electron-energy-loss spectroscopy (HREELS) (Ref. [15]) have concluded that the surface structure involves two types of molecules in a c4×2 unit cell when the alkyl chain is long enough (while the unit cell is $\sqrt{3} \times \sqrt{3}R30°$ for a short chain) (Fig. 1). It is so when van der Waals interactions between chains become larger than the Au(111)-S interaction. They favor an arrangement of the chains similar to that in bulk solid alkanes, where the carbon planes of adjacent molecules form a herring bone structure.[10] Details of the molecular conformations of the two molecules were not obtained, but the x-ray diffraction study showed that *S* atoms dimerize on the Au(111) surface. From this finding it was suggested that the molecules are L shaped, implying gauche C-C bonds near the substrate. A similar conclusion was drawn from the analysis of the SFG CH_3 band azimuthal anisotropy.[12] A sketch of a possible structure is shown in Fig. 2. Two quantitative pieces of information concerning this structure were provided by x-ray diffraction: the distance between nearest S atoms of 2.2 Å, which corresponds to the distance between a bridge and a threefold hollow site, and the angle of the tilt plane (which contains the C backbone, tilted with respect to the
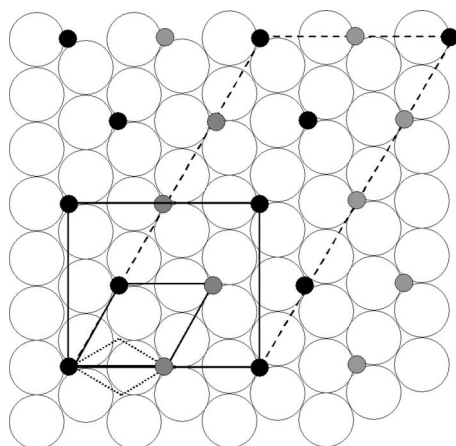
FIG. 1. Schematic view of the unit cells relevant to alkanethiols on Au(111). The large open circles are the gold atoms. The Au(111) and the $(\sqrt{3} \times \sqrt{3})R30°$ unit cells are shown in dotted and solid lines, respectively. Methyl groups, which are lifted and shifted above the Au plane at the end of the alkyl chains, are still located on a $(\sqrt{3} \times \sqrt{3})R30°$ lattice (small circles). However the black and gray circles correspond to different heights, implying that the unit cell is $c(4 \times 2)$ (broken lines). The methyl surface structure can be alternatively described using the $(3a \times 2a\sqrt{3})$ [or $p(3 \times 2\sqrt{3})$] rectangular unit cell [with a the Au(111) lattice constant] (rectangle in solid lines). According to Ref. 10 S atoms are not arranged on the same lattice (see Fig. 2).

surface normal, as shown in Fig. 2). The rest of the structure was not characterized. In particular, important pieces of information are lacking, such as the relative orientation of the planes of the C backbones of adjacent molecules, which is important for van der Waals interactions and for the bonding geometry of the terminal group, the Au-S-C angle which is indicative of the hybridization of the S orbitals, and the dihedral angles about the first CC bond, which corresponds to a loss of energy with respect to the trans conformation, compensated by the gain in the Au-S bonding.

The continuing interest for SAMs has stimulated recent calculations[16] and experiments[17,18] on alkanethiols, leading to suggestions concerning the bonding of the molecules. For very small chains (1 and 3 C atoms) and at low coverage, it was concluded from STM experiments and density-functional theory (DFT) calculations that S atoms are not bound directly to Au(111) but to Au adatoms, the most stable surface species being CH_3S-Au-SCH_3. These adatoms would be provided by the lifting of the Au reconstruction induced by the adsorption of the alkanethiols. Using normal incidence x-ray standing waves (NIXSW), a similar suggestion of bonding to adatoms was done for longer chains (6 and 8 C atoms) and ramified chains [tertiary butylthiolate $(CH_3)_3CS$ which forms a different phase as may be expected from the larger size of the molecules].

The commonly admitted opinion that the absence of the CH_2 groups in SFG implies an all-trans conformation would lead to rejection of the proposition of L-shaped molecules. However, as pointed above, this opinion is not rigorously justified. Therefore, we have developed a model that allows to calculate the SFG spectrum of all CH stretching modes for any conformation of the alkyl chain.[19] We made the assump-
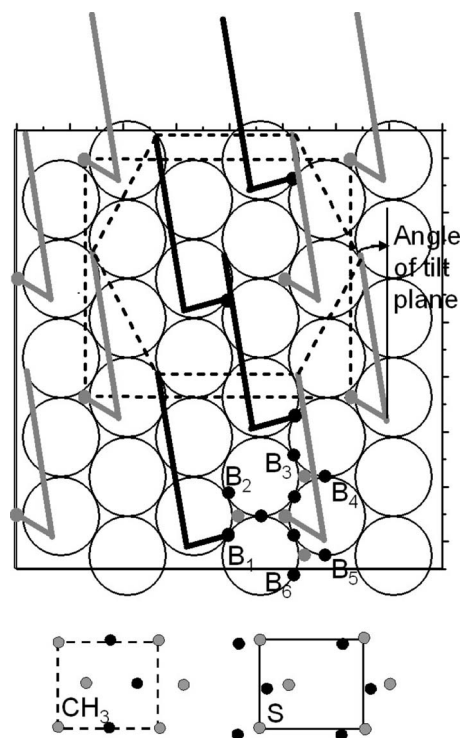

FIG. 2. Top-view sketch of the surface structure proposed in Ref. 10. Two types of conformations (black and gray) coexist. Each of them exhibits a gauche defect near the surface, resulting in an L shape to account for the pairing of S atoms at a distance of 2.2 Å while the C backbones must remain at a much larger distance to optimize attractive van der Waals interactions. The $(3a \times 2a\sqrt{3})$ unit cell is recalled in dotted lines, together with the hexagons formed by the methyl groups. For clarity the patterns of CH_3 groups and S atoms in the unit cell are shown as insets. A second quantitative information provided by Ref. 10 is the angle of the tilt planes (containing the C backbones) with respect to the raw of Au atoms. Also displayed around the adsorption site of the molecule located down and on the right are the nearest threefold hollow (gray) and bridge sites (black), and the six bridge sites $B_1 - B_6$ (black) located 2.2 Å away.

tion that CH_2 stretching modes are local, and we have calculated *ab initio*[20,21] the hyperpolarizability tensor components of CH_2 and CH_3. The $v=1$ state of the CH_3 symmetric stretching mode is strongly perturbed by a Fermi resonance with $v=2$ of the bending mode. We have taken this into account by redistributing the calculated (unperturbed) intensity according to the weight of the perturbing state in the wave function of the $v=1$ state. This weight can be extracted directly from the experimental intensity ratio of the two interacting states, using a relationship specific to SFG and different from the case of absorption.[19] We have tested this model against the intensity alternation of CH_3 modes as a function of alkyl chain length. For chain lengths above 14,[10] changing the chain length by one CH_2 group does not change the bonding to the substrate and weakly modifies the strength of van der Waals lateral interactions to the neighboring alkyl chains. Therefore each time a CH_2 group is added to the chain the methyl orientation with respect to surface normal alternates between two values, the C backbone orientation

remains unchanged. Our model allowed reproduction of this effect.[19] For this test of the model, the conformation of the alkyl chain was assumed all trans. In this work, we use our model to investigate whether the experimental SFG spectra are compatible with and allow to obtain the detailed conformation of the two types of L-shaped molecules suggested in the literature[8–12] and sketched in Fig. 2. The degrees of freedom in the calculation of SFG spectra are the four angles defining the direction of bonds around the S and the two C atoms nearest to the substrate. The restriction to four angles is due to the facts that the conformation around C atoms is tetrahedral and that the chain is all trans except around the first CC bond. The implication of the possible presence of Au adatoms will also be discussed.

II. EXPERIMENTAL

Several SAMs of octadecanethiol (ODT) were prepared in different places and by different people. The preparation procedure of SAMs is described in Refs. 6 and 19. The substrate of ODT is a polycrystalline gold film deposited on quartz and annealed in a hydrogen flame. AFM images show randomly oriented (111) crystallite facets of size $1-2$ μm. Our broad band SFG setup[22] is detailed elsewhere.[6,23,24] Tunable IR pulses (4 μJ, 145 fs, and 150 cm^{-1} bandwidth) and "visible" pulses (800 nm, 2 μJ, and Fourier limited duration corresponding to an adjustable bandwidth of a few cm^{-1}) are superimposed on the sample in a collinear, copropagating configuration at an incident angle of ≈ 50 or 60° in p polarization. The reflected SFG signal is detected after a monochromator on a cooled charge coupled device (CCD) camera. The monochromator is usually used with a resolution of ≈ 4 cm^{-1}, but the resolution can be improved down to 0.4 cm^{-1} at 650 nm, which is obtained when the entrance slit has the size of one single pixel. In practice the spectrum resolution is limited by the visible beam bandwidth, which is decreased until the spectrum does not change.

III. EXPERIMENTAL RESULTS

The SFG spectrum of the SAM of ODT and other alkanethiols has been reported several times in the literature.[4,5,19,22,25] It exhibits three strong bands at the methyl frequencies. By contrast, no band was reported at the frequencies of CH$_2$. We are interested in this paper to understand the reason for this absence of the CH$_2$ modes and to know whether its calculated intensity can bring information about the molecular conformation. The absence of the CH$_2$ bands cannot be due to the all-trans conformation of the alkyl chain in itself because as explained in Sec. I there is at least one unpaired CH$_2$ group in ODT. From the experimental point of view, we need to know if the intensity is strictly zero. We have searched for the CH$_2$ bands across a series of spectra recorded under the best possible conditions. We find that depending on the experimental parameters such as the center frequency of the IR laser, the quality of the signal to noise ratio, and the stability of the laser between the recordings of the spectra of the sample and the reference, the CH$_2$ symmetric mode can indeed be observed, while the CH$_2$
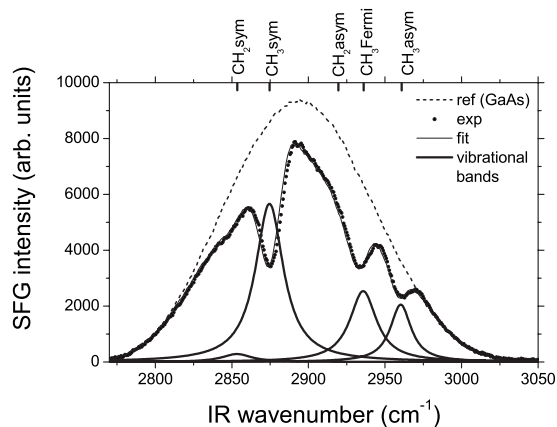

FIG. 3. Experimental SFG spectrum of ODT, showing that the CH$_2$ symmetric stretching mode and its Fermi resonance are indeed present although very weak (see text). The CH$_2$ asymmetric stretching mode is not detectable. Also shown are the reference SFG spectrum recorded on GaAs which gives the spectral shape of the IR laser, the fit of the spectrum to formula (1), and the deconvolution of the spectrum into four Lorentzians.

asymmetric mode was never seen. Figure 3 shows a SFG spectrum of ODT in which a weak band at the frequency of the CH$_2$ symmetric mode is observed. Such an observation may be expected in two situations: when the quality of the spectrum is very good, allowing the observation of very weak bands; or when the sample lacks order, resulting in more defects in the chains and more CH$_2$ groups able to contribute to the signal. In the latter case however a (not observed) weakening of the CH$_3$ bands with respect to better samples would occur due to a broader orientation distribution of the CH$_3$ groups. We conclude that in the best spectra the CH$_2$ symmetric stretch is above the detection limit, and we use this below to quantify the upper limit of its intensity with respect to that of the CH$_3$ modes.

The vibrational bands are superimposed on a nonresonant signal arising from the gold surface which has the spectral shape of the IR laser. To separate the vibrational bands from the nonresonant background, the spectrum is fitted to the following formula:[12,26]

$$I(\omega_{SF}) \propto g(\omega_{ir}) \left| \chi_{NR} + \sum_\nu \frac{A_\nu e^{i\phi_\nu}}{\omega_{ir} - \omega_\nu + i\Gamma_\nu} \right|^2 . \quad (1)$$

The IR laser spectral profile $g(w_{ir})$ is measured independently by SFG from a reference GaAs sample. χ_{NR} is the Au nonresonant response. A$_\nu$, φ_ν, ω_ν, and Γ_ν are the amplitude, phase (with respect to the non resonant contribution), frequency, and half width of mode ν. There are four parameters for each band, but two of them (the frequencies and widths) are known, allowing to verify that the fitting routine does not return unphysical values. In the fitted spectrum of Fig. 3, four Lorentzians were first used in the fit. The spectrum exhibits three strong bands at the frequencies of the methyl symmetric stretch (2875 cm^{-1}), asymmetric stretch (2964 cm^{-1}), Fermi resonance of the symmetric stretch (2936 cm^{-1}),[7] and one weak band at the frequency of the symmetric CH$_2$ stretch (2853 cm^{-1}). When one attempts to

TABLE I. Tensor components calculated *ab initio* for the four vibrational modes. *ijk* stands for $\chi_{ijk} \equiv \alpha_{ij}\,\mu_k$. Indexes refer to the local frames (Fig. 4): for CH_3 z is the symmetry axis, and for CH_2 the symmetry axis is in the yz plane. The two CH_3 modes are split into in-plane and out-of-plane modes.

CH_3 sym	$xxz = -1.38$	$yyz = -1.44$	$yzz = 0.13$	$zyz = 0.13$	$zzz = -1.11$
CH_3 asym in plane	$xxy = -1.36$	$yyy = 1.87$	$yzy = -1.56$	$zyy = -1.56$	$zzy = -0.13$
CH_3 asym out of plane		$xyx = -1.13$	$xzx = -1.54$	$yxx = -1.13$	$zxx = -1.54$
CH_2 sym	$xxz = 1.07$	$yyz = 0.72$	$yzz = 0.38$	$zyz = 0.38$	$zzz = 0.46$
	$xxy = 1.52$	$yyy = 1.02$	$yzy = 0.54$	$zyy = 0.54$	$zzy = 0.64$
CH_2 asym		$xyx = 1.29$	$xzx = 0.91$	$yxx = 1.29$	$zxx = 0.91$

fit the spectrum with an additional band (Fig. 3), the quality of the fit is improved and the fitting routine returns the frequency of 2891 cm^{-1}, which is attributed in the literature to a band in Fermi resonance with the symmetric CH_2 stretch.[7] The CH_2 asymmetric stretch (2918 cm^{-1} for an ordered SAM) is indeed too weak to be detectable. This shows that the symmetric CH_2 stretch is just above the detection limit, which explains why it was not reported before and shares its intensity with a Fermi resonance (such as the symmetric CH_3 stretch), while the asymmetric CH_2 stretch is below the detection limit. Note that the present calculations confirm the lower intensity of the asymmetric CH_2 mode with respect to the symmetric mode for all calculated molecular conformations. The intensity (A_ν^2/Γ_ν^2) ratio $s2/s3$ of the symmetric CH_2 to symmetric CH_3 stretch bands is therefore not strictly zero. Only an upper bound can be evaluated ($s2/s3 < 0.1$, taking into account the presence of the Fermi resonance) due to the small intensity of the bands. The band intensities derived from the fits are very sensitive to the spectral shape of the IR laser, which must be recorded with precision. In addition, the shape of the bands depends sensitively on the phase. This allows to determine the phase from the spectra. However we find a rather large dispersion ($\approx 10\%$) of the measurements (intensity and phase) because the phase of one band influences the next band. To improve the precision, we have averaged a series of measurements (several locations on several samples while varying the focus of the laser beams) at a precisely measured incidence angle (60°).

IV. SPECTRUM MODELING

Details of the model are provided in Ref. 19. The hyperpolarizability tensors of the modes of individual CH_2 and CH_3 groups are calculated *ab initio* in a suitable frame *ijk*. All CH_2 groups are assumed to have the same hyperpolarizability tensor: there is no feature in the spectra that can be ascribed to specific CH_2 groups (such as those adjacent to CH_3 or to S). The tensor elements β_{ijk} are calculated in the following harmonic approximation:[20,21]

$$\beta_{ijk} \propto \sum_\nu \frac{\langle 0|\alpha_{ij}|v\rangle \langle v|\mu_k|0\rangle}{\omega - \omega_v + i\Gamma}$$

$$\approx \sum_\nu \frac{1}{2m\omega_\nu(\omega - \omega_\nu + i\Gamma_\nu)}\left(\frac{\partial \alpha_{ij}}{\partial Q_\nu}\right)\left(\frac{\partial \mu_k}{\partial Q_\nu}\right), \qquad (2)$$

where α_{ij} is the Raman polarizability tensor component, μ_k

is the dipole moment component, Q_ν is the local mode, and m is the corresponding reduced mass. Because the SAM is highly ordered with a large part of the alkyl chain all trans (that is to say with a mirror plane), we calculate the derivatives of α and μ in the propane molecule, the simpler alkyl chain with a mirror plane (the C plane). As a result the calculated hyperpolarizabilities of the in-plane and out-of-plane CH_3 asymmetric modes are slightly different. Q_ν contains only the appropriate displacements of the CH bonds related to the CH_2 group or to one of the two CH_3 groups. For Γ_ν we use the experimental width. The nonvanishing tensor components are listed in Table I. We emphasize that in this model we neglect the influence of R and R' on the hyperpolarizability of R-CH_2-R' because this effect is expected to be much smaller than the cancellation of signals due to a locally trans conformation and their vanishing due to the very weak fields in the surface plane.

The components χ_{IJK} of the molecular hyperpolarizability tensor in the surface frame *IJK* are obtained as the sum of the individual β_{IJK}, which are obtained from the β_{ijk} by appropriate frame transformations $U_{A/B,IJKijk}$,[27]

$$\chi_{IJK} = \sum_{molecules} \sum_{vib.modes} \beta_{IJK} = N_A \sum_{vib.modes} \sum_{ijk} U_{A,IJKijk}\beta_{ijk}$$

$$+ N_B \sum_{vib.modes} \sum_{ijk} U_{B,IJKijk}\beta_{ijk}. \qquad (3)$$

Subscripts A and B correspond to the two types of molecular conformations with surface densities N_A and N_B. The $U_{A/B,IJKijk}$ designate a collection of rotations. Euler angles define successively the orientation of $C_{(0)}H_2$ with respect to the Au surface and the Au-S bond of $C_{(i+1)}H_2$ with respect to $C_{(i)}H_2$ and of CH_3 with respect to $C_{(16)}H_2$ (where C atoms are numbered from 0 near the substrate to 17 in CH_3). Angles are defined in Fig. 4. Along the all-trans part of the chain ($C_{(2)}$ to $C_{(17)}$), Euler angles are determined by the tetrahedral environment around C atoms and by the all-trans conformation. Near the surface, the environment about S is not tetrahedral and the conformation about $C_{(0)}$ and $C_{(1)}$ is not assumed to be trans: there remain four undetermined angles to describe the geometry of the alkyl chain (Fig. 4), which are the azimuth of the $SC_{(0)}$ bond α_{SC}, the Au-S-$C_{(0)}$ angle α_S, and the dihedral angles ψ_0 and ψ_1 about S-$C_{(0)}$ and $C_{(0)}$-$C_{(1)}$, respectively. ψ_1 is the angle that corresponds to possible gauche defects at the bottom of the chain. After taking into account the incidence angles, the polarization of laser beams,
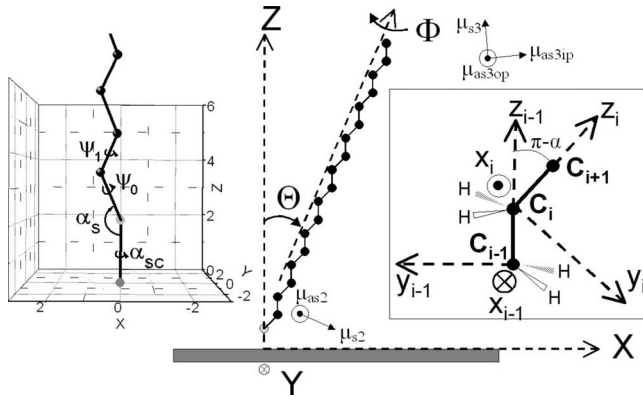
FIG. 4. Definition of the angles that characterize the molecular conformation. Θ and Φ are the molecular tilt and twist angles. Note the arbitrary choices of the C plane (XZ) and of the orientation of the CH_2-CH_3 bond. The directions of the dipole moments of CH_3 (symmetric μ_{s3}, asymmetric in-plane μ_{as3ip} and out-of-plane μ_{as3op}) and CH_2 (symmetric μ_{s2} and antisymmetric μ_{as2}) are also indicated. Left inset: angles defining the geometry at the bottom of the alkyl chain. Right inset: local frames. z_i is along $C_{(i)}C_{(i+1)}$, $y_i z_i$ is a mirror plane for $C_{(i)}H_2$ and x_i is parallel to HH. Euler angles relating $x_{i-1}y_{i-1}z_{i-1}$ and $x_i y_i z_i$ (about z_{i-1}, the rotated x_{i-1}, and z_i, successively) are $(0, \pi\text{-}\alpha, \pi)$ in the all-trans conformation, with α as the tetrahedron angle. Near the substrate Euler angles are successively $(\alpha_{SC}, \pi\text{-}\alpha_S, \pi)$, $(\psi_0, \pi\text{-}\alpha, \pi)$, and $(\psi_1, \pi\text{-}\alpha, \pi)$. The symmetry axis of $C_{(17)}H_3$ is z_{16}.

and the optical indexes in the framework of a three-media optical model (air, molecular layer, and gold substrate)[28] an effective scalar hyperpolarizability may be defined (and compared to the experimental A_ν);

$$\chi^{(2)}_{\text{eff}}(\omega_{SF}) = [\mathbf{L}(\omega_{SF}) \cdot \mathbf{e}_0(\omega_{SF})]^T$$
$$\cdot \boldsymbol{\chi}^{(2)}(\omega_{SF}):[\mathbf{L}(\omega_{ir}) \cdot \mathbf{e}_0(\omega_{ir})][\mathbf{L}(\omega_{vis}) \cdot \mathbf{e}_0(\omega_{vis})].$$
$$(4)$$

$\boldsymbol{\chi}^{(2)}$ is the hyperpolarizability tensor of components χ_{IJK}. The superscript T means the matrix transpose, $\mathbf{e}_0(\omega_i)$ is the unit vector of the electric field at frequency ω_i in vacuum, and $\mathbf{L}(\omega_i)$ are Fresnel tensors. The optical indexes used in the calculation are listed in Ref. 19. We integrate the hyperpolarizability tensor over the sample azimuth to account for the polycrystalline nature of our sample. We must also take into account the Fermi resonance to derive a quantitative information from the intensity of the CH_3 symmetric stretching mode: the band in Fermi resonance borrows its intensity from that of the main band. As stated in Sec. I, it was shown that the transfer of SFG intensity from the main band to the Fermi resonance can be treated phenomenologically: the experimental intensity ratio between the main band and the Fermi resonance allows to calculate the mixing coefficient of the states in resonance, which in turn allows to relate the experimental intensity (perturbed by the Fermi resonance) to the calculated intensity (which does not take into account the Fermi resonance).[19]

The model calculates all angles that describe the chain geometry. As explained above, the all-trans, tetrahedral geometry from $C_{(2)}$ to $C_{(17)}$ restricts the number of degrees of freedom to four (α_{SC}, α_S, ψ_0, and ψ_1). Other angles are useful to discuss band intensities and are unambiguously determined by α_{SC}, α_S, ψ_0, and ψ_1. They are the "global" molecular tilt Θ of the all-trans part of the chain axis with respect to the surface normal, the twist Φ of the carbon backbone about the chain axis, and tilt_{CC}, tilt_{CH3}, and tilt^0_{CH2}, tilt^1_{CH2}, tilt^2_{CH2}, the angles defining respectively the tilt with respect to the surface normal of the $C_{(15)}C_{(16)}$ bond, of the symmetry axis of CH_3 (which is along the $C_{(16)}C_{(17)}$ bond) and of the symmetry axis of CH^i_2, with obvious notations where the superscript i designates the number of the CH_2 group.

V. MOLECULAR ORIENTATION AND METHYL ORIENTATION

It is natural to draw the molecule from bottom to top using α_{SC}, α_S, ψ_0, and ψ_1 successively, as Fig. 4 would suggest. However, the procedure used to derive the conformation is the opposite: Θ and Φ are derived first from the methyl intensities, then ψ_1 is obtained from the methylene intensity and from the available pieces of information on surface structure. Angles α_{SC}, α_S, and ψ_0 are calculated from Θ, Φ, and ψ_1.

The orientation of the C plane and of the methyl group of ODT was obtained in Ref. 19 together with that of pentadecanethiol (PDT). PDT spectra were recorded to increase the constraints on the model. Θ and Φ are determined from the comparison of the CH_3 asymmetric to symmetric intensity ratio $as3/s3$ with the calculated $as3/s3$ (Θ, Φ). As recalled in Sec. I, the intensity alternation as a function of chain length was taken into account in Ref. 19: ODT and PDT have the same Θ and Φ angles but an odd and even number of CH_2 groups, respectively, and therefore different tilt_{CH3} angles. Figure 5 shows the dependence of the methyl tilt angle tilt_{CH3} on Φ for selected values of Θ and the variation in the $as3/s3$ intensity ratio with tilt_{CH3}. Three types of molecular orientations were found compatible with the SFG spectra:

(i) Assuming a single type of molecule, the best tilt, twist angles were found to be $\Theta=30°$ and $\Phi=290°$.[19] The corresponding data points in Fig. 5 are labeled ODT and PDT.

(ii) If two conformations are assumed to coexist on the surface, they must have the same Θ and presumably different Φ. Let us write $\Phi=\Phi_0 \pm \delta\Phi$. The case of $\Phi_0=0$ corresponds to two molecules images of each other with respect to the tilt plane; their dipole moments make the same angles with respect to the surface normal, resulting in identical azimuth-averaged spectra. Therefore symmetry implies that the combination of the two conformations $\Theta=30°$ and $\Phi=\pm 290°$ corresponding to (i) is in agreement with SFG spectra.

(iii) If two conformations with $\Phi_0 \neq 0$ are assumed, $\delta\Phi$ characterizes the angle between the C planes. In Ref. 19 it was found that the best fit to SFG spectra is obtained for $\Theta=30°$, $\Phi_0=290°$, and $\delta\Phi=45°$, corresponding to perpendicular C planes. In what follows, molecules with $\Phi=245$ and $335°$ will be called "A" and "B," respectively. The $as3/s3$ ratio depends directly on the tilt angle of the methyl group with respect to surface normal (tilt_{CH3}). The inset of Fig. 5 shows how tilt_{CH3} depends on the molecular twist

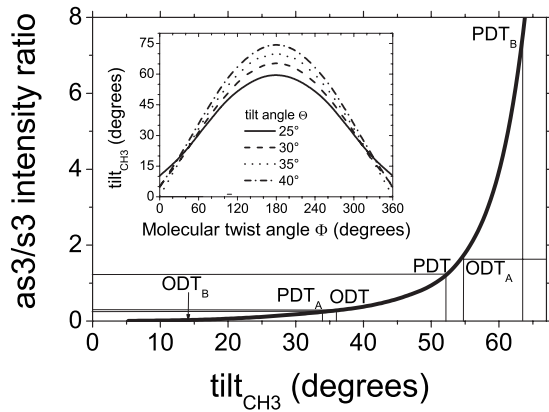FIG. 5. Calculated ratio of the asymmetric to symmetric SFG intensities as3/$s3$ as a function of the tilt angle tilt$_{CH_3}$ of the CH_3 symmetry axis with respect to the surface normal. The molecular tilt angle is $\Theta = 30°$. To allow direct comparison between ODT and PDT, the ratios are actually A_{as3}/A_{s3} which are independent of the linewidth variations from one spectrum to the other. Labels at the crossing of horizontal and vertical lines indicate the points corresponding to experiment: ODT and PDT in the case where the spectrum is attributed to a single molecule, ODT$_{A/B}$ and PDT$_{A/B}$ in the case of two types of molecules. Inset: relationship between the tilt of the methyl group and the molecular twist angle for a molecular tilt angle between 25 and 40°.

angle Φ. Figure 5 shows the as3/$s3$ intensity ratios of A and B molecules alone and of the two together. A range of $(\Theta, \Phi_0, \delta\Phi)$ solutions exists if ODT spectra are taken in consideration alone. However, a single solution is compatible with ODT and PDT together. In what follows we will see if these molecules, A and B, can be L shaped.

VI. CONFORMATION NEAR THE SURFACE

Once Θ and Φ are determined from the comparison of the as3/$s3$ ratio with experiment, we only need to find ψ_1 to obtain the entire molecular geometry. A gauche defect, characterized by ψ_1, is necessary to obtain an L shape and the pairing of S atoms on the surface. As ψ_1 varies the $C_{(0)}$-S bond rotates about the average molecular axis. To a given value of ψ_1, it corresponds a position of S above the surface, characterized by α_S (the Au-S-$C_{(0)}$ angle, with Au-S being normal to the surface), α_{SC} (the azimuth of the SC bond with respect to the tilt plane), and ψ_0 (the dihedral angle about the SC$_{(0)}$ bond). The value of ψ_1 is constrained by four factors.

A. Steric hindrance within the molecules

It is well known that three dihedral angles about a C-C bond are energetically favored because they minimize steric hindrance, in the present case between (Au)-S-($C_{(0)}H_2$) and $-(C_{(1)}H_2)-(...)-(C_{(17)}H_3)$. With our definitions of angles, the preferred angles are $\psi_1 = 0°$, corresponding to the lower energy trans conformation (which is adopted by the molecule along the rest of the C chain), and $\psi_1 = 120$ and $240°$, the two gauche conformations which correspond to second minima of the energy (+0.035 eV with respect to trans according to textbooks in the case of butane). The
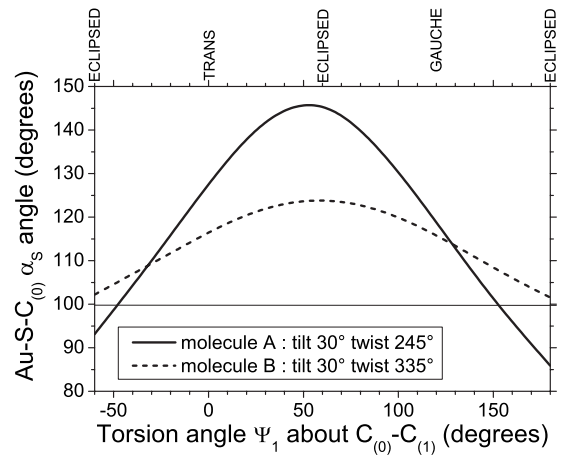
energy maxima are for eclipsed conformations [$\psi_1 = 60°(+0.14 \text{ eV}), 180°(+0.2 \text{ eV}), \text{ and } 300°(+0.14 \text{ eV})$ for butane]. The deviation of the molecules from the trans conformation is possible providing that more energy is gained in the Au-S bond and S-S pairing than lost by a gauche defect. The actual ψ_1 angle may not be accurately 120 or 240°. The range of acceptable values for ψ_1 depends on the (unknown) energy balance between the gain in the Au-S bond and the loss in the S-$C_{(0)}$-$C_{(1)}$-$C_{(2)}$ bonds.

B. Steric hindrance between the molecules and the surface

Because molecules are tilted, the S atom can be above $C_{(0)}$ for a certain range of values of ψ_1. The height of S on the surface is determined by the Au-S bond length of 2.4 Å. The height of $C_{(0)}$ depends on that of S and on ψ_1. That $C_{(0)}$ goes below S is of course unphysical because part of the molecule would then "touch" the surface. The Au-S-$C_{(0)}$ angle α_S must remain larger than $\approx 100°$ (Ref. 29) to minimize the steric hindrance between the molecule and the surface. Figure 6 displays the acceptable range of values of ψ_1 (defined by $\alpha_S > 100°$) for molecules A and B. It shows that only one (120°) of the two gauche defects is possible.

C. SFG spectrum

The $s2/s3$ ratio must remain below the experimental upper bound. When ψ_1 varies, the tilt$_{CH_2}^0$ angle of the unpaired $C_{(0)}H_2$ group nearest to the surface also varies, resulting in a change in $s2/s3$ ($CH_2^{(0)}$ has a different alignment than all other CH_2 groups when $\psi_1 \neq 0$). Because the surface is metallic, the electric fields are much smaller in the surface plane (tilt$_{CH_2}^0 = 90°$) than along the surface normal (tilt$_{CH_2}^0 = 0°$). The SFG response is undetectable when the dipole moment lies in the surface plane. In Ref. 19 it was found that the main trends of the calculated variation in the SFG intensity of the CH_3 bands are understandable on the basis of the orientation of the IR dipole moment (while the Raman transition moment does not induce clear features as a function of
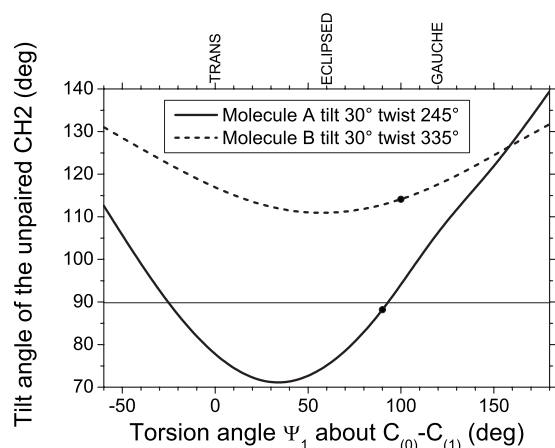

FIG. 6. Variation in the Au-S-$C_{(0)}$ angle α_S as a function of the angle ψ_1 about the $C_{(0)}$-$C_{(1)}$ bond for molecules A and B. The straight horizontal line recalls that steric hindrance implies that $\alpha_S > 100°$.

FIG. 7. Variation in the $\text{tilt}^0_{\text{CH2}}$ angle, characterizing the orientation of the IR dipole moment of the unpaired CH_2 group with respect to surface normal, as a function of the dihedral angle about the $C_{(0)}$-$C_{(1)}$ bond, for A and B molecules. The line at $\text{tilt}^0_{\text{CH2}}=90°$ indicates the angle for which the SFG signal is zero for the CH_2 symmetric stretch. The dots correspond to the best values of ψ_1.

molecular orientation). Figure 7 shows the variation in $\text{tilt}^0_{\text{CH2}}$ for molecules A and B as a function of ψ_1. For molecule A, the IR dipole moment lies in the surface plane for $\psi_1=93$ and

$-25°$ and it is never close to the surface normal, suggesting that the $s2$ intensity cannot be very large. For molecule B the range of values accessible to $\text{tilt}^0_{\text{CH2}}$ is more restricted and $\text{tilt}^0_{\text{CH2}}$ varies between 111 and 131°.

The way molecules A and B contribute to the CH_2 (and CH_3) band intensities is illustrated in Figs. 8 and 9. In the two figures Θ, Φ_A, and Φ_B are the same (implying the same intensities of the CH_3 bands), the value of ψ_1^B is 100°, while ψ_1^A is chosen to minimize ($\psi_1^A=30°$ in Fig. 8) or maximize ($\psi_1^A=-60°$ in Fig. 9) the intensity of CH_2 bands. The corresponding conformations are intermediate between trans and eclipsed (30°) and eclipsed ($-60°$), respectively. The contributions of A and B molecules cancel when their IR dipole moments point symmetrically above and below the surface plane (Fig. 8). Figure 9 also shows that the CH_2 asymmetric stretch can be visible for certain conformations. However in all cases we find it smaller than the symmetric stretch, which is consistent with the experimental situation where it is not observed while the symmetric stretch is just above the detection limit.

Figure 10 shows an example of the dependence of the $s2/s3$ intensity ratio as a function of ψ_1^A for $\psi_1^B=100°$. It can be substantially larger (0.25) than the experimental upper bound (0.1), in particular for the nominal value of the gauche defect ($\psi_1^A=120°$). This shows that there are two possibilities
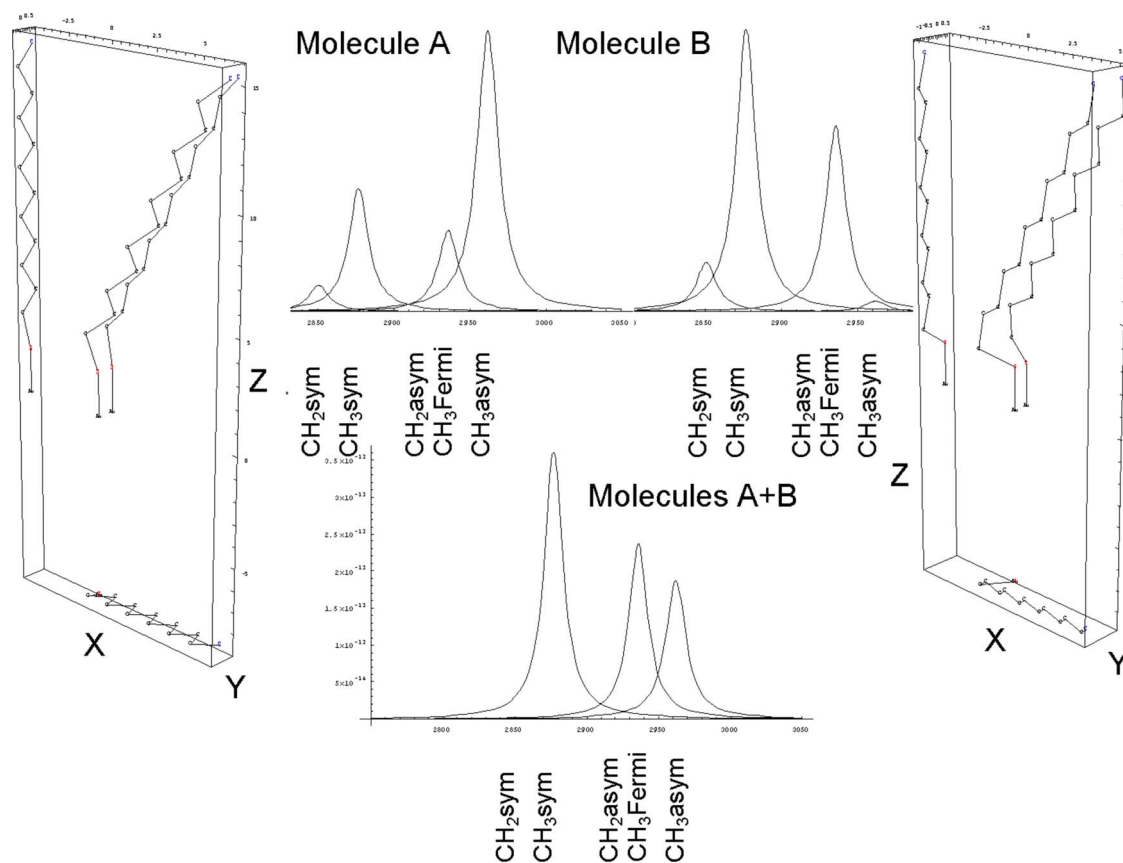

FIG. 8. (Color online) Example of calculated molecules and their SFG spectra, where the contributions of the two molecules to the CH_2 symmetric stretch cancel. Molecule A: tilt $\Theta=30°$, twist $\Phi^A=245°$, $\psi_1^A=30°$ (conformation intermediate between trans and eclipsed), and $\text{tilt}^0_{\text{CH2}}(A)=71°$. Molecule B: tilt $\Theta=30°$, twist $\Phi^B=335°$, $\psi_1^B=100°$ (nearly gauche), and $\text{tilt}^0_{\text{CH2}}(B)=114°$. The IR dipole moment of the unpaired CH_2 point by 29° above and 24° below; the surface plane in molecules A and B, respectively. Their contributions to the SFG spectrum cancel. Note that for clarity the length of the molecules is 12 instead of 18.
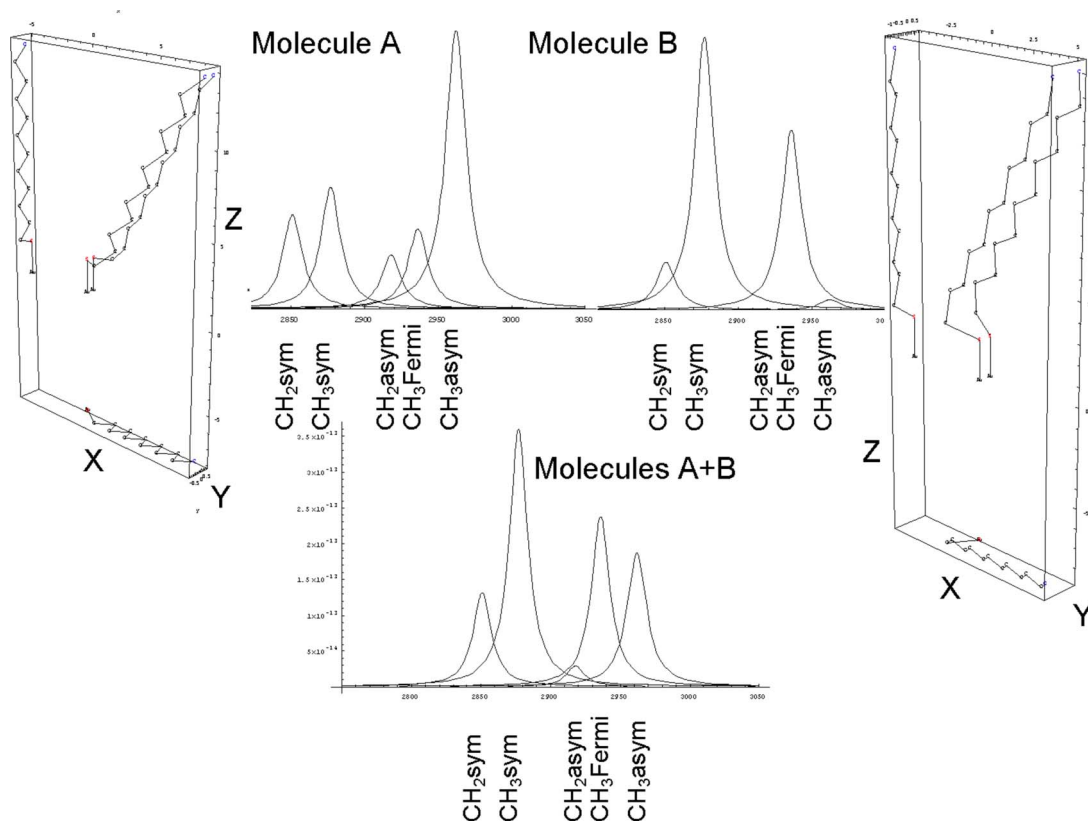
FIG. 9. (Color online) Example of calculated molecules and their SFG spectra, where the contributions of the two molecules to the CH_2 symmetric stretch add up. Molecule A: tilt $\Theta = 30°$, twist $\Phi^A = 245°$, $\psi_1^A = -60°$ (eclipsed conformation), and $\text{tilt}_{CH2}^0(A) = 113°$. Molecule B as in Fig. 10: tilt $\Theta = 30°$, twist $\Phi^B = 335°$, $\psi_1^B = 100°$ (nearly gauche), and $\text{tilt}_{CH2}^0(B) = 114°$. The unpaired CH_2 have almost the same orientations in the two molecules, and their contributions to the SFG spectrum add up. Note that for clarity the length of the molecules is 12 instead of 18.

for molecule A: the all-trans conformation and a distorted (90°) gauche conformation. Similarly, for molecule B we find that the molecule can be all trans or gauche (100°). The best possible angles minimizing $s2/s3$ are found to be ψ_1^A

$= 90°$ and $\psi_1^B = 100°$ (two L-shaped molecules) (Fig. 11).

D. Surface structure

Having calculated molecular conformations compatible with the SFG spectra and physically sound from the point of
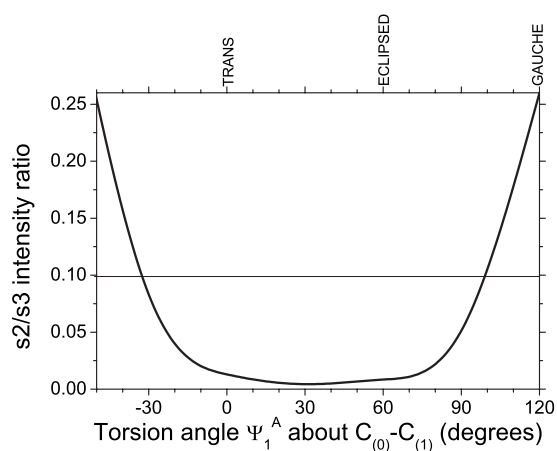

FIG. 10. Case of two molecules with perpendicular C planes ($\Theta = 30°$, $\Phi^A = 245°$, and $\Phi^B = 335°$): calculated intensity ratio $s2/s3$ of the CH_2 symmetric stretch to CH_3 symmetric stretch modes as a function of the dihedral angle ψ_1^A about the $C_{(0)}C_{(1)}$ bond of molecule A for $\psi_1^B = 100°$. The variation in $s2/s3$ as a function of ψ_1^B assuming $\psi_1^A = 90°$ is similar.

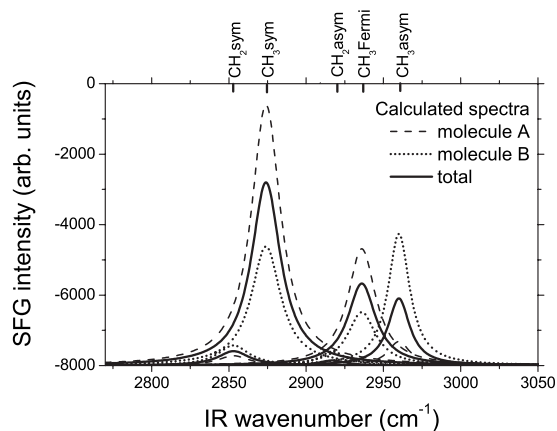FIG. 11. Calculated spectra of A and B molecules for the appropriate angles characterizing the L shape: $\Theta = 30°$, $\Phi^A = 245°$, $\Phi^B = 335°$, $\psi_1^A = 90°$, and $\psi_1^B = 100°$. Three spectra are shown, corresponding to molecular conformations A alone, B alone, and A and B together. The angle of incidence is 60°.
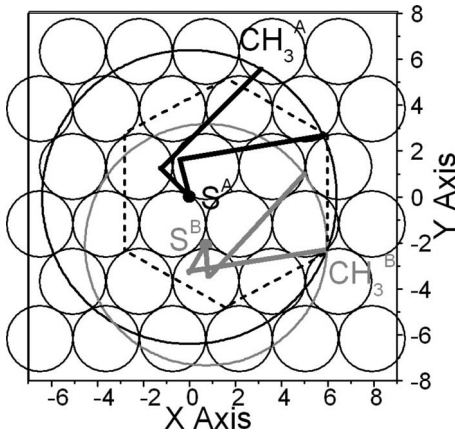
FIG. 12. Sketch of molecules A and B for two orientations of the tilt plane (the plane that contains the average tilted C backbone). Atoms S^A and S^B are adsorbed on well defined sites of Au(111) (bridge for A and threefold hollow for B). The positions of the methyl groups depend on the molecular conformations and on the orientation of the tilt plane. They must fall on the hexagon in dashed lines [the size of which is given by the Au(111) structure, but the position of which with respect to Au(111) depends on the molecular conformations]. The degree of freedom to accommodate the molecule simultaneously on the Au(111) sites and on the hexagon is the rotation of the tilt plane.

view of steric hindrance, we must check that they can be arranged on the available sites of Au(111). Indeed the molecules cannot fit onto the Au(111) lattice in all cases. In the $3a \times 2a\sqrt{3}$ structure the CH_3^A and CH_3^B groups are located in an hexagonal array (Fig. 2).[13] The S^A atoms "fall" naturally onto a second lattice which is translated with respect to the first one along CH_3^A-S^A, but it is not granted that the S^B atoms fall on real adsorption sites of this lattice when molecules A and B do not the same geometry. The system has one degree of freedom, namely, the rotation of the tilt plane with respect to the surface lattice (Fig. 12). When the tilt plane rotates, $CH_3^{A/B}$ groups rotate about the corresponding $S^{A/B}$ atom, along a circle of radius equal to the projected molecular length of molecule A/B in the surface plane. The correct angle if it exists is the one for which CH_3 groups

form regular hexagons (Fig. 12). In practice, to find out if the combination of A and B molecules can fit into the surface structure, we keep CH_3^A and CH_3^B fixed, we rotate the molecules, we assume that S^A is in one of the adsorption sites, and we calculate the distance between S^B and the second site as a function of the rotation angle. The experimental information available from Ref. 10 is the distance between S^A and S^B, not the actual sites. Therefore this calculation has to be done for all the possible combinations of adsorption sites compatible with the S^A-S^B distance. For example, shown in Fig. 2 are the six bridge sites that may correspond to one threefold hollow site. For $\psi_1^A = 90°$ and $\psi_1^B = 100°$ we find that a rotation of the tilt plane of 9° allows to adsorb the molecules on Au(111) with B molecules in threefold sites and A molecules in the B_1 bridge site of Fig. 2. The accuracy of the coincidence of the molecule with its adsorption site is 0.07 Å. The rotation angle of the tilt plane compares satisfactorily with the experimental value of 8°.[10] Therefore our model allows to find a solution compatible with all available experimental data.

Finally we must pay attention to the other conformations consistent with the spectra, where at least one molecule is all trans. There is a total of four, numbered from #1 to #4 (Table II). (i) The first three ones are based on the single type of all-trans molecule of paragraph five, characterized by ($\Theta = 30°$ and $\Phi = 290°$) for which $s2/s3 = 0.03$ (#1) and two derivatives of it. (ii) The first one is the symmetric $\pm\Phi$ combination of paragraph five, section (i) ($\Theta = 30°$ and $\Phi = \pm 290°$) (#2), characterized by the same $s2/s3$ ratio as #1 and at an angle of 40° between C planes. The second one is a combination of one gauche ($\Theta = 30°$, $\Phi = +290°$, and $\psi_1 = 110°$) and one all trans ($\Theta = 30°$ and $\Phi = -290°$; $\psi_1 = 0°$) molecule (#3). In this last case, the angle between C planes is also 40° and $s2/s3 = 0.07$. The geometries with a gauche defect on each chain (ψ_1^A or $\psi_1^B \approx 120$ and 240°) result in too high $s2/s3$ or too small α_S: only one of the molecules can be L shaped. In addition, the two all-trans molecules corresponding to ($\Theta = 30°$ and $\Phi = 290° \pm 45°$) (#4) are also compatible with SFG spectra as was already mentioned (Fig. 10). The search for an appropriate combination of threefold and bridge sites and rotation of the tilt plane revealed that none of the combination of all-trans molecules (#1, #2, and #4)

TABLE II. Main properties of the five solutions consistent with the SFG spectra.

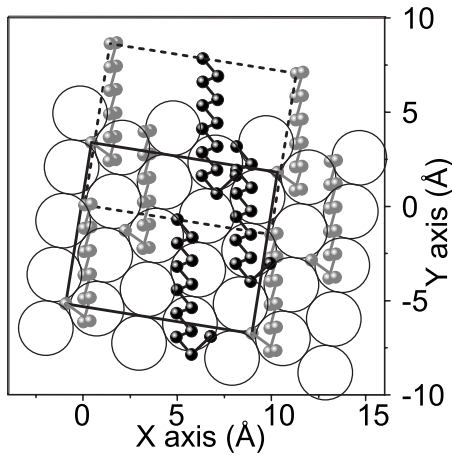|		Θ	Φ	ψ_1	Angle between C planes	Fit into surface structure	Rotation of tilt plane
			1 type of molecule				
#1	1 all trans	30°	290°	0°		No	
		2 molecules with the all-trans part of the chain symmetric with respect to the tilt plane					
#2	2 all trans	30°	$\pm 290°$	0°	40°	No	
#3	1 all trans +1 L shaped	30°	$\pm 290°$	110/0°	40°	Yes	Incorrect (59°)
		2 molecules with perpendicular C planes					
#4	2 all trans	30°	245/335°	0/0°	90°	No	
#5	2 L shaped	30°	245/335°	90/100°	90°	Yes	Correct (8°)

FIG. 13. Top view of the conformations and arrangement of A (black) and B (gray) molecules in the $(3a \times 2a\sqrt{3})$ unit cell. The *YZ* plane is the tilt plane. The rectangle in dotted lines is the unit cell in the plane of the CH_3 groups. The rectangle in bold lines is the unit cell in the plane of the S atoms. To keep the figure as simple as possible, H atoms are not shown, and the number of C atoms is 12 instead of 18.

can fit with the surface structure: the S^B atom falls at 2.2 Å at best from its target adsorption site. The reason is of course that the nearly straight shape of the all-trans molecules cannot allow to bring the two S atoms close while maintaining the all-trans part of the alkyl chains at the distance appropriate for van der Waals interactions. By contrast molecules #3 can be arranged in threefold and bridge sites with an accuracy of 0.05 Å. However the rotation of the tilt plane in this case is found to be 59°, far from the experimental value.

VII. DISCUSSION

Perspective and top views of the surface structure that fits with all structural information are shown in Figs. 13 and 14, respectively, and a view along the average chain axis is shown in Fig. 15. Figure 15 shows that the rotation of the C planes produces a structure similar to, but different from the herring bone structure which is adopted in the solids of alkanes. In fact the structure cannot be the herring bone with the arrangement of the molecules of Fig. 2. Mar and Klein[30] computed the energy of various structures involving two molecules with perpendicular C planes using molecular-dynamics calculations. They found a difference of only a fraction of kcal/mole. The energy related to surface bonding brings much more energy into the system and may easily result in a structure different from the herring bone.

The quantitative details of the conformations are given in Tables II and III. The comparison with the results of the literature is limited to the tilt angle Θ of the molecules and to the Au-S-CH_2 angle α_S. The values found previously for Θ are 30° for chain lengths of 16 and 18 from x-ray diffraction,[10] 27° (Ref. 31) to 34° (Ref. 32) from reflection absorption infrared spectroscopy studies, and 32° on the basis of the area available on the surface per molecule.[1] Thus SFG provides a reasonable value for Θ. α_S is 128 and 120°
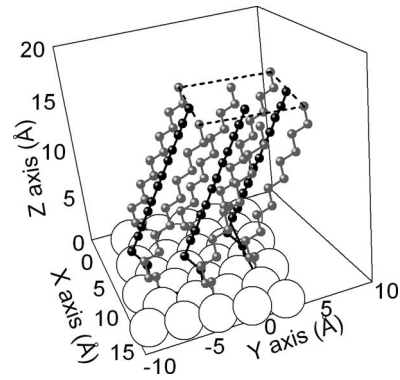

FIG. 14. Perspective view of the molecules. The perspective is chosen to show that the C planes of molecules A and B are perpendicular. Other details are like in Fig. 13.

for molecules A and B. The value of α_S cannot be guessed with certainty because orbital hybridization about the S atom is subject to vary significantly with the number and type of atoms about S. α_S was set to 100° in molecular-dynamics calculations.[31] Recently it was found to be 117.3 and 123.6° for SCH_3 on relaxed and unrelaxed Au surfaces using DFT calculations,[16] showing that our values of 128 and 120° are quite reasonable.

The other angles characterizing the conformations were not determined before. The validity of our modeling is supported by the precision of the positioning of the molecules in the surface structure proposed by Ref. 10 (distance of molecule B from its ideal adsorption site; rotation angle of the tilt plane). In addition, it is also important to emphasize that the molecular conformations do not depend abruptly on the parameters used in the calculations. We have investigated how stable the solution is when one modifies, e.g., α with respect to the tetrahedron angle, the amplitude of certain elements of the hyperpolarizability tensor, and other parameters. We find that the molecular angles must be changed slightly but without changing the basic molecular shape. Even ignoring the redistribution of the intensities due to Fermi resonance does not produce catastrophic results in terms of the general shape of the molecules.

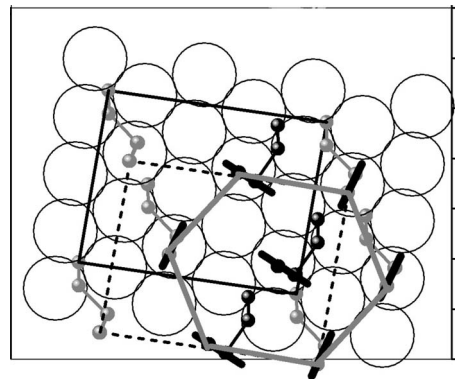

FIG. 15. View of the molecules along the average chain axis. Other details are as in Fig. 13. A hexagon formed by the CH_3 groups is also shown in bold gray lines, and the planes formed by the C backbones are materialized by a bold black line.

TABLE III. Other angles defining the geometry of the different solutions compatible with the SFG spectra.

#	ψ_1^A/ψ_1^B	Tilt$^{A/B}$	Twist$^{A/B}$	Tilt$_{CH3}^{A/B}$	Tilt$_{C0H2\text{-}C1H2\text{-}C2H2}^{A/B}$	α_S^A/α_S^B	$\alpha_{SC}^A/\alpha_{SC}^B$	ψ_0^A/ψ_0^B
1	0	30	290	35	98-82-98	131	46	32
2	0/0	30/30	290/−290	35/35	98-82-98/98-82-98	131/131	46/−46	32/−32
3	110/0	30/30	290/−290	35/35	106-82-98/98-82-98	120/131	172/−46	37/−32
4	0/0	30/30	245/335	54/14	78-102-78/117-63-117	146/116	69/16	115/13
5	90/100	30/30	245/335	54/14	88-102-78/114-63-117	128/120	133/−126	59/11

The results shown above demonstrate that more information can be obtained from SFG spectra than previously reported. In the present case of complex molecules, the spectrum analysis is possible because the number of the angular degrees of freedom is strongly reduced by the knowledge that the largest part of the alkyl chain is all trans. Because the system remains multidimensional, a stepwise approach is needed to determine the angles that characterize the conformations. The angles that are appropriate for a methodic search turn out to be first the overall molecular tilt and twist angles which allow to determine the as3/s3 ratio of the methyl bands, and second the torsion angle about the first CC bond, which determines the s2/s3 ratio of the methylene symmetric band with respect to that of the methyl. It is critical to take the conformation as a whole and to calculate all bands together. The calculation of CH_2 intensities is indeed useful—and necessary—in spite of the fact that the CH_2 bands are near the limit of detection: the constraint on CH_2 orientation imposed by the SFG intensities is strong enough to derive the molecular conformation. We calculate that CH_2 bands of all-trans molecules are detectable if the chains are tilted enough and that in L-shaped molecules they may be undetectable due to the particular combination of molecular orientation and cancellation between two types of molecules. These results show that the absence of CH_2 bands is not strictly equivalent to an all-trans conformation, although this is very often read in the literature.

Taking into account not only the SFG spectra but also the available pieces of information about surface structure leads to a unique solution and allows to obtain the rotation angle of the tilt plane which we find close to the value determined by x-ray diffraction. The interest of SFG is that it provides a complete description of the molecules (Tables II and III), including important information which was lacking until now, in particular the orientation of the C planes which are found perpendicular with respect to each other and the Au-S-C angle (α_S), which is an indicator of the hybridization of the S orbitals, important for quantum calculations.

If the knowledge of surface structure was not available, the azimuth-averaged SFG spectra used here would allow to propose several structures. However, SFG spectra can allow a better discrimination between the different structures if they can be measured on a single crystal. Au single crystals cannot be used routinely because most SAMs are normally obtained in the liquid phase, and series of samples are in general needed to optimize the sample preparation. Thin Au films deposited on glass are used most often. It is therefore important to realize that even azimuth-averaged spectra can be useful to obtain information on molecular conformation.

However the use of single crystals would allow to account for the variation in the spectra with sample azimuth. In the present case of alkyl chains the conclusion of two types of adsorption sites and two coexisting molecular conformations was drawn from the measurement of SFG as a function of azimuth,[12] independently of the x-ray and He diffraction experiments.

The conclusion of this work is that SFG is compatible with the hypothesis of two types of L-shaped molecules adsorbed in a combination of threefold and bridge sites. As mentioned in Sec. I, the other recent suggestion of the literature is that the molecules occupy fcc and fcp threefold sites, with the S atoms being bonded to Au adatoms. This conclusion seems well established for a low coverage of very short molecules (up to three C atoms).[16] For larger coverages, only middle size chains (up to eight C atoms) were studied,[17] whereas it is known that the structure becomes independent of chain length above 12.[10] More work, perhaps comparing the two adsorption models (two L-shaped molecules vs Au adatoms) on a same set of diffraction data, seems necessary to conclude between the two interpretations. In the hypothesis that Au adatoms would remain stabilized by alkyl thiols even at saturation coverage, the molecular arrangement has additional degrees of freedom with respect to the case of a flat Au(111) surface (the Au-Au-S bond orientations). Presumably there is no need to assume any gauche defect on the $C_{(0)}$-$C_{(1)}$ bond because there is enough flexibility in the Au-Au-S bonds for the molecules to adopt a shape that satisfies simultaneously the requirements of the surface structure and the intermolecular van der Waals interactions. Our finding that #2 and #4 arrangements of all-trans molecules are consistent with SFG spectra indicates that SFG cannot be the basis to reject the hypothesis of Au adatoms. Presumably arrangement #4 would be preferred because it minimizes steric hindrance between alkyl chains.

VIII. CONCLUSION

This work shows that the hypothesis of two L-shaped molecular conformations coexisting in the ODT SAM is in agreement with SFG spectra. Our spectrum modeling based on a full calculation of the CH_3 and CH_2 modes in the local mode approximation and taking into account the geometry of the entire molecule allows to determine the detailed conformation of the two molecules (Figs. 13–15). The conformations are physically sound, with the C planes of adjacent molecules perpendicular to each other as in the solid of ODT, with the molecular tilt angle and the orientation of the tilt plane in agreement with the literature and reproducing the

intensity alternation with chain length. This shows that our approach provides a satisfying tool to investigate the conformation of alkyl chains. It is so because SFG selectively probes the important parts of the molecules, namely, where they depart from the all-trans conformation, while IRAS averages the contributions of all CH_2 modes and other techniques are only sensitive to one of the two ends of the molecules. The local mode approach[7] is essential to explore the whole range of possible conformations. Although it is very rare that a surface science technique allows to derive the entire surface structure by itself, the question that arises is: to what extent can SFG be used alone to determine molecular structures? Azimuth averaged SFG spectra are compatible with several conformations, and the combination of SFG with other surface science tools allows to determine the right structure. In this work, we have been able to choose among the SFG compatible solutions by taking into account the information on the methyl group surface structure (from STM experiments) and on the pairing of S atoms in threefold and bridge sites (from x-ray diffraction experiments). Our analysis brings in turn further information, in particular the relative orientation of C planes and the bonding configuration about S atoms. Although many applications of SAMs are clearly not in UHV, the study of single crystals, avoiding average on azimuth, would greatly help to choose among solutions, as was shown by Yeganeh *et al.*[12] who concluded on the only basis of the azimuthal dependence of SFG that two types of molecules are present.

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