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Sum-frequency vibrational spectroscopic study of mixed alkylsiloxane monolayers self-assembled on fused silica surface

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Abstract

Self-assembled monolayers of fluorinated and non-fluorinated alkylsiloxanes were prepared on fused silica substrates and studied by both conventional IR and nonlinear sum-frequency vibrational spectroscopy complemented with XPS. Simultaneous self-assembly of the two alkylsiloxanes results in preferential adsorption of the fluorinated compound and formation of the mixed monolayer. Different species are found to be closely coadsorbed in the mixed monolayers which distinguishes self-assembly from Langmuir–Blodgett deposition where the similar species tend to separate into different phases. Nonlinear sum-frequency spectroscopy of C–H stretching region detects symmetry perturbations of the alkyl chain induced by *trans–cis* defects and partial fluorination and clearly distinguishes between them. All three characterization methods consistently indicate the presence of a hydrocarbon residue in all deposited monolayers, which is ascribed to the hexadecane used as a solvent during the self-assembly process. © 1997 Elsevier Science S.A.

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1. Introduction

The ability to modify properties of various surfaces was always essential for numerous practical applications. Deposition of self-assembled thin films has proven to be a convenient way of achieving this goal [1]. It was found, that unique surface properties, e.g. low friction can be obtained if the deposited film had an ordered structure [2]. At present, two major techniques for the ordered films deposition have developed: Langmuir–Blodgett deposition and self-assembly. Langmuir–Blodgett deposition involves creation of the thin film on a liquid subphase with the subsequent transfer of the formed film onto the substrate. While this process is better studied and understood, it has its limitations; mainly the difficulties of the technical implementation and the inability to perform deposition on the substrates with non-flat surfaces. Self-assembly of the amphiphilic molecules on the surfaces from the solution was found to be a competitive alternative to the Langmuir–Blodgett process [3]. The film is formed by dipping the substrate into the bulk solution. A compact ordered structure of the film is provided by the cohesive interaction between the molecules during adsorption and in some cases, by the ordered structure of the adsorption sites on the substrate [4]. Such structure makes the very first deposited monolayer so oleo- and hydrophobic that the adsorption stops on this stage. While being attractive from the practical point of view, self-assembly deposition imposes more limitations on the choice of the substrate and the adsorbate than the Langmuir–Blodgett technique. Thus the study of new substances capable of self-assembly is essential.

At the moment, the most widely studied groups of self-assembling molecules are carboxylic acids and their salts, alkanethiols and alkylsiloxanes. In particular, the alkylsiloxane self-assembled monolayers (SAMs) were successfully formed on such substrates as fused silica, oxidized silicon, glass and mica. Covalent siloxane bonding to the substrate ensures high mechanical, chemical and thermal stability of alkylsiloxanes compared to the other monolayers mentioned above. In addition, silane molecules are believed to be cross-linked with the siloxane bonds on the surface forming a two-dimensional network. This further improves the film stability. Various recent studies, e.g. [5], have

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shown that the alkylsiloxane monolayers were highly ordered and compact. However, the resulting surface properties, e.g. wettability, appeared to be quite similar if silanes with ordinary alkyl chain are used [6]. Modification of the surface properties could be achieved by mixing silanes with the different tail groups. For example, it was found that the alkylsilanes with fluorinated chain also self assemble on the similar substrates resulting in extremely low surface energy [7]. Fluorinated alkylsiloxane monolayers were also deposited with Langmuir–Blodgett (LB) technique [8] and showed lower values of dry friction in comparison with the non-fluorinated alkylsiloxane SAMs. However, in the LB mixed films separate phases of fluorinated and non-fluorinated species were found on the surface. Also, only a 1:1 mixture of components was studied.

Performing this study, we were challenged to prepare an alkylsiloxane monolayer of binary composition by self-assembly and find out if different species could be mixed in arbitrary proportions, allowing for continuous adjustment of surface characteristics. We have prepared and investigated mixed SAMs of both fluorinated and non-fluorinated alkylsilanes with the same chain length and head groups. This ensured a consistent observation of the changes in alkylsilane self-assembling behavior induced by the chain fluorination.

Monolayer samples were prepared on fused silica substrates. Two main surface probes were used for sample characterization: XPS and sum-frequency vibrational spectroscopy. Transparent substrates also made it possible to record the vibrational spectra of the monolayers by the conventional FTIR spectroscopy in transmission mode. The C–H stretching region was investigated.

2. Experimental

The alkylsiloxane samples were prepared on double-sided optically polished flat fused silica substrates, $10 \times 10 \times 1$ mm, which were cleaned by washing in organic solvents and 20 min treatment in hot Piranha solution ($H_2O_2/H_2SO_4 = 4:1$). After that, the substrates were rinsed in the deionized water, dried under nitrogen flow and kept in ozone atmosphere for not more than 1 h before deposition.

Octyltrichlorosilane ($CH_3(CH_2)_7SiCl_3$) and its fluorinated analog, (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane ($CF_3(CF_2)_5(CH_2)_2SiCl_3$) were used. It is important to note that the alkyl chain of the latter was not completely fluorinated with two methylene groups still present next to the silicon atom. The alkylsiloxane films produced from these two silanes are designated here as C8H and C8F. Some samples were prepared using octadecyltrichlorosilane (OTS) and are referred to hereafter as C18H.

Trichlorosilanes were dissolved in either an 80:20 mixture of hexadecane/carbon tetrachloride or in pure hexadecane (Aldrich). Mixed films were deposited from the mixed solutions of different silanes. The total silane concentration was always kept close to 2.5 mM. All chemicals were used as received.

The samples were prepared by dipping of the cleaned substrates into the trichlorosilane solution for 20 min at ambient temperature. The deposition was performed in standard test-tubes purged with dry nitrogen to reduce the rate of silane hydrolysis in the solution due to the atmospheric humidity. After the deposition the samples were rinsed with carbon tetrachloride. The samples of the fluorinated alkylsiloxanes occasionally required wiping of the organic residue from the surface. Finally, the samples were dried in a nitrogen flow and baked for 1 h at 100°C.

XPS measurements were performed with the VG-ESCA CLAM-2 hemispherical energy analyzer. A MgKα X-ray source was used. The samples were completely covered with X-ray beam. The electron emission angle was close to 90° in respect to the surface plane. Survey spectra were recorded with 1 eV steps within 0–1000 eV range, 100 eV pass energy; the individual peak spectra with 0.1 eV steps and 50 eV pass energy. The instrument resolution in the latter regime was 1.2 eV. No X-ray-induced decomposition of the investigated films during the acquisition was detected. To eliminate the charging of the insulating fused silica substrate, a flood gun was used. The peak positions of C(1s), Si(2p) and O(1s) transitions were kept close to 285, 103 and 533 eV.

Vibrational spectra of alkylsiloxane films were obtained using sum-frequency generation (SFG) spectroscopy. This second order non-linear technique may be considered a combination of the Raman and IR spectroscopies. In fact, the sum frequency signal is an anti-Stokes signal, which is coherently intensified by the resonant pumping of the probed transition in infrared. When the IR frequency coincides with the resonance in the medium, the sum-frequency generation efficiency is enhanced. As a result, a vibrational spectrum can be recorded if the IR frequency is continuously tuned. The second frequency is usually visible, since in that case generated sum-frequency light is also visible and a single-photon sensitive detector (PMT) can be used.

Due to the combined IR–Raman nature of SFG, only the transitions with non-vanishing IR and Raman activity can be detected. While seemingly restrictive, this selection rule causes SFG spectra to be less complicated than corresponding Raman and IR spectra. Furthermore, as we intend to show here, various structural perturbations in the probed medium can make formerly inactive transition to appear in the SFG spectrum, and thus make the particular perturbation easily detectable.

Since SFG is a second-order non-linear process, no signal (in electro-dipole approximation) could be generated in the fused silica substrate, which is a centrosymmetric medium, and its non-linear susceptibility χ^2 equals zero [9]. Hence, in our case the SFG signal is generated only in the surface layer. It is also known [10] that χ^2 is an orientational average over single molecule non-linear polarizabilities. For the film on the surface this average is non-zero only if the

molecules of the film are ordered. Thus, the existence of SFG response from the surface of the fused silica indicates that ordered film is present on it. In this paper we plot SFG spectra using SFG *strength* which is the square root of the SFG intensity because the latter is proportional to the square of χ^2, and consequently to the square of the surface concentration.

The SFG spectrometer used in this study consisted of a 1.06 μm Nd–YAG mode-locked laser (Continuum PY61C, 40 mJ at 35 ps, 20 Hz repetition rate) as a main pumping source, a LBO frequency doubler as a visible light source and a $LiNbO_3$ parametric oscillator as a source of the tunable IR. Visible and infrared beams were focused onto the sample down to spot diameters of 0.1 mm for IR and 0.5 mm for visible light. The respective energies were 1 and 0.25 mJ. To suppress unwanted contribution from the visible light scattered from the sample surface, emerging sum-frequency radiation was spatially filtered and passed through the combination of a holographic notch filter and a monochromator. P-polarization of infrared and s-polarization for both visible and sum-frequency radiation with respect to the sample plane (*ssp* combination) was used, unless specified otherwise. The sum-frequency radiation was detected with the Hamamatsu R955 photomultiplier. The frequency scale for the IR source was calibrated with a standard polystyrene film.

For purpose of comparison, the vibrational transmission-absorption spectra of the monolayers were recorded using BOMEM-100 FTIR spectrometer with a liquid nitrogen cooled InSb detector at 4 cm^{-1} resolution. Spectra were referenced with a clean freshly ozone-oxidized fused silica substrate.

3. Results and discussion

3.1. XPS characterization

We begin with the XPS characterization of all studied samples; relevant data are summarized in the Table 1. The XPS spectrum of non-fluorinated C8H sample shows peaks arising from the aliphatic carbon, silicon and oxygen. No response from the chlorine was detected in all of the investigated samples, indicating that the hydrolysis of the alkyltrichlorosilane during the deposition was complete. XPS spectrum of the sample with the monolayer differs from the one of the cleaned substrate mainly in the C(1s) peak strength (peak area); the latter appears to be 6-times higher for the C8H sample.

Table 1

XPS peak areas, normalized to O(1s)

Sample	C(1s) C–H	C(1s) C–F	F(1s)	O(1s)	Si(2p)
C8H	0.1609	–	–	1	0.2024
C8F	0.0684	0.0598	0.6305	1	0.1939
1:5	0.0913	0.0399	0.4302	1	0.2105
1:8	0.0954	0.0124	0.1922	1	0.2056
Clean substrate	0.0344	–	–	1	0.1743

XPS spectrum of C8F monolayer shows additional peaks that are all due to fluorine, namely F(1s) and F_{KLL}. The spectra of the mixed samples show similar fluorine features, decreasing with the decrease of the fluorinated compound content in the deposition solution (see Table 1). This indicates that the film deposition from the mixed solution indeed results in a mixed structure on the surface.

Si(2p) and O(1s) peak intensities data for the C8H monolayer and the clean substrate can be utilized to estimate the film thickness. Photoelectrons originating from the oxygen and silicon atoms have to penetrate through the compact layer of the alkyl chains. The resulting attenuation should be different due to different kinetic energies of photoelectrons. Hence, the Si(2p) and O(1s) peak ratio should be different for the clean substrate and for the sample with a monolayer. This is indeed seen from the last column of Table 1: the ratio changes from 0.17 to 0.20 with the deposition of the film.

The photoelectron attenuation length in aliphatic layers as a function of the kinetic energy was experimentally obtained by Bain et al. [11]. Given the energy of 1253.6 eV (magnesium Kα source) and binding energies of 103 and 533 eV for the Si(2p) and O(1s) transitions, respective kinetic energies are around 1150 eV for Si(2p) electrons and 720 eV for O(1s) electrons. The corresponding attenuation lengths are 3.4 and 2.1 nm. Fitting the Si(2p):O(1s) ratios data to the ratio of relevant exponents gives an estimate for the film thickness of 0.9 nm. Given the known aliphatic monolayer thickness per CH_2 group of 0.128 nm, the C8H monolayer should be about 1.0 nm thick. This result is in good agreement with our estimate indicating that we have indeed deposited a film with a thickness close to one monolayer. It is seen from Table 1 that the Si(2p):O(1s) ratio is around 0.20 for all samples with the monolayers within 5% error, meaning that the attenuation of O(1s) photoelectrons in these samples is also close. Thus the O(1s) intensity was used as a reference for comparison of the XPS data from different monolayers.

For all samples containing C8F, C(1s) transition appears as a doublet with a second peak around 290 eV (see Fig. 1). This peak apparently originates from the fluorine-bonded carbon [12]. In the study of a similar fluorinated monolayer [8], a similar structure in the C(1s) region was observed and even the contribution from CF_2 and CF_3 was resolved. This was possible because the emission was detected at an acute angle of 15° in respect to the surface. We were unable to achieve such sensitivity with the emission angle close to surface normal. Comparison of the data for pure C8F sample with the data for the sample produced from the mixed solution with a fluorinated/non-fluorinated compounds ratio of 1:5 yields a ratio of F(1s) intensities of 0.68, and a ratio of C(1s) (289 eV) intensities of 0.67; i.e., F(1s) and C(1s) (289 eV) peaks change synchronously with changing of the fluor-

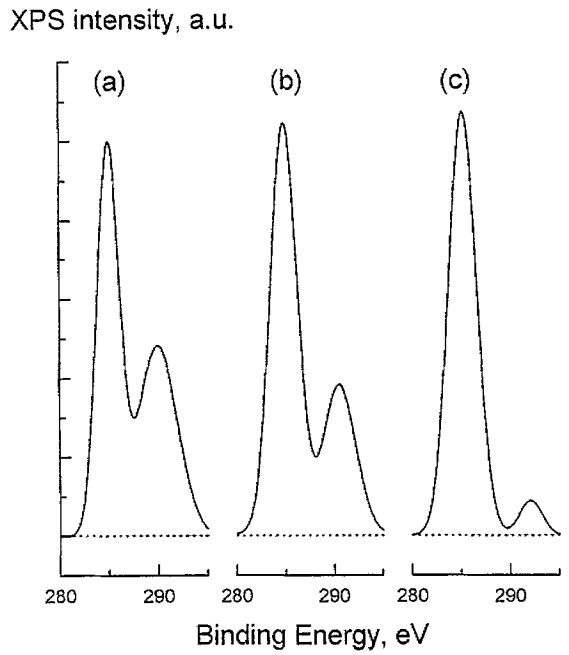

Fig. 1. C(1s) peaks referenced by O(1s), multiple Gaussian fit, for pure C8F monolayer (a), 1:5 sample (b), and 1:8 sample (c).

ine content. Since the fluorine and fluorine-bonded carbon are present in the C8F only, these ratios apparently reflect the ratio of C8F contents between the samples. We now note (Table 1) that the total intensity of the C(1s) doublet is similar for all samples with C8F (0.12, 0.13, 0.10 for C8F, 1:5, 1:8 samples, respectively). This means that the degree of the surface coverage for these samples is also close. As a result, the ratios of C(1s) (289 eV) and F(1s) peaks between the mixed and pure C8F samples are also a measure of the C8F content in a given mixed monolayer.

Our data show that the 1:5 mixture of components in the deposition solution (16% of the fluorinated compound) produces a layer with the fluorine and fluorine-bonded carbon content of 68% with respect to the pure fluorinated film. Hence, the relative C8F content in the mixed monolayer is about 4-times higher than in the deposition solution. A similar estimate for 1:8 sample (11% of fluorinated species) gives 21% C8F content in the monolayer from 289 eV C(1s) peaks ratio and 30% from F(1s) peaks ratio. The observed discrepancy is most likely due to the relatively low signals from C8F species. In any case, these results demonstrate that the fluorinated silane is preferentially adsorbed form the mixed solution.

In a study by Banga et al. [13] it was found that the fluorinated octyltrichlorosilane forms a compact monolayer about 10-times faster than the non-fluorinated OTS (octadecyltrichlorosilane). However, different deposition solutions and silanes of different chain length were used. In our case the comparison is much more consistent, since the two silanes with the same chain length were deposited from the mixture and preferential adsorption of the fluorinated silane was still observed. We have checked if a substitution mechanism was the reason for the observed imbalance. A series of samples was prepared by consecutive dipping into solutions of the pure compounds without intermediate baking. It was found that the monolayer corresponding to the first solution was always deposited. Thus it seems unlikely that the fluorinated silane is capable of replacing the non-fluorinated one already adsorbed on the surface.

The observed shift of the adsorption equilibrium may be explained by the faster adsorption speed resulting from the faster hydrolysis rate of fluorinated compound in the solution, in accord with previous results [13]. But it is important to realize that the hydrolysis rate is not the only factor influencing the adsorption rate. Stronger cohesive interaction between the fluorinated alkyl chains may contribute as well, as it is known [14] that the long-chain amphiphiles self-assemble faster. The known helical conformation of a fluorinated alkyl chain [15] could also be of importance.

The peak ratio in the C(1s) doublet reflects the ratio of the fluorine-bonded and hydrogen-bonded carbon in the film. From the stoichiometry, this ratio should be $R_1 = 3.0$ and $R_2 = 1.01$ for pure C8F and 1:5 samples, respectively. The value for R_2 is obtained based on 70% fluorinated species content in the 1:5 sample which in turn was derived from the F(1s) peak data as described above. However, the experimental values for R_1, R_2 and R_1/R_2 are quite different from the calculated ones, namely $R_1 = 0.87$, $R_2 = 0.44$ and $R_1/R_2 = 1.98$. Since we have shown that the 289 eV C(1s) peak is a consistent measure of the fluorine content in a monolayer, we conclude that a significant amount of hydrocarbon residue is present on the surface of the samples. A simple calculation shows that the experimental values for the relative intensities of C(1s) doublet in the spectra of C8F, 1:5 and 1:8 samples can be explained, if from five to six hydrogen-bonded carbon atoms are present per one monolayer molecule.

The most likely source of detected hydrocarbon residue is hexadecane, used as a solvent during the monolayer deposition. We have found that hexadecane is readily adsorbed on a clean fused silica substrate and is not removed by our standard post-deposition cleaning procedure. The sample dipped into hexadecane and rinsed with CCl_4 has shown a C(1s) peak 2.4-times stronger than the control clean sample. Aliphatic carbon content in the hexadecane-contaminated sample was found to be about half of that in the C8H monolayer. The latter estimate is consistent with the amount of residue measured for the samples with monolayers.

However, the mechanism of the hydrocarbon inclusion in the monolayer could be different from the one, responsible for the adsorption on the clean substrate. Numerous studies (see [16] and references therein) have proved that the molecules with straight alkyl chains can be easily intercalated between the molecules of the monolayer during deposition. Up to one monolayer of hexadecane was reported to be coadsorbed in a layer with OTS. The amount of the aliphatic residue (assuming hexadecane as an origin) in our experiments with eight carbon chain length silanes is somewhat

lower, about one hexadecane molecule per three molecules of the monolayer. We have found the same amount of residue in the C8F and mixed samples. This means that hexadecane is equally well entrapped between both C8H and C8F chains, despite the fact that there is little conformational similarity between the flat hexadecane and helical C8F molecules. It seems likely that hexadecane can occupy voids between fluorinated chains because the latter have a bigger cross-section than the ordinary alkyl chains. The same amount of residue in all monolayers with the different C8F content (as low as 20% for the 1:8 sample) suggests also that a pure C8H monolayer should contain a comparable amount of stray hydrocarbons.

3.2. Vibrational spectroscopy

SFG and FTIR scans of all samples were recorded in the 2600–3400 cm^{-1} range. Pronounced resonances were found, however, only in the C–H stretching area (2800–3000 cm^{-1}). No response from hydroxyl groups was detected around 3400 cm^{-1}. The latter fact indicates that not only the hydrolysis of the chlorosilane, but also the subsequent condensation of the alkoxysilane on the surface was close to complete.

The major vibrational spectroscopy results are presented in Fig. 2. SFG spectra of the C8H and C18H (OTS) monolayers (top graph) show two major peaks of the methyl symmetric stretching mode at 2875 cm^{-1}, a Fermi resonance of the symmetric methyl stretch and the overtone of the methyl bending mode at 2940 cm^{-1} [17]. Antisymmetric methyl stretch is known to be absent from the SFG spectra of aliphatic monolayers recorded with the particular combination of incident and detected radiation [10], used in our study.

Contrary to the methyl vibrations, methylene stretches are usually absent in the SFG spectra [18]. Part of the long alkyl chain built of the methylene groups in *trans*-configuration is nearly centrosymmetric and does not contribute to the second-order non-linear susceptibility $\chi^{(2)}$. However, if the *trans*-configuration is lost, the center of symmetry is gone and methylene vibrations appear in the SFG spectrum. For example, methylene vibrations were observed in SFG experiments with a loosely packed aliphatic layer on the water surface [10]; they were shown to disappear after the film was compressed and the *trans*-chain configuration became favorable.

Methylene stretches at 2950 and 2920 cm^{-1} are indeed present in our SFG spectra, but are much more pronounced for the short-chain C8H than for the long-chain C18H(OTS) monolayer. This fact is not surprising, since short-chain aliphatic monolayers are likely to be more disordered than the long-chain ones. Such a lack of ordering may be a result of the weaker cohesive interaction between the shorter chains.

The SFG spectrum of the C8F sample is plotted in the middle part of Fig. 2. Except for the standard *ssp* (SFG, visible, IR) polarization combination, only the *ppp* polarization combination was found to produce detectable spectrum. The *ppp* SFG spectrum was essentially identical to *ssp*, albeit about 2-times weaker. Despite the absence of the methyl group in the fluorinated C8F chain, there is some response at methyl stretching frequencies around 2875 cm^{-1} and 2950 cm^{-1}. This could arise from the hydrocarbon residue intercalated in the monolayer and detected earlier by XPS. The strongest feature in the spectrum at 2920 cm^{-1} coincides with the antisymmetric methylene stretching mode. This mode is readily observed in the IR spectra of both C8H and C8F monolayers plotted in Fig. 2 (bottom). Note that the SFG and FTIR spectrometers were calibrated independently and the frequency coincidence was not artificial.

While the C8F monolayer is not completely fluorinated and contains two methylene groups, the appearance of methylene stretches in its SFG spectrum shows that the central symmetry of the $-CH_2-CH_2-$ unit in the chain is lost. Surprisingly, only antisymmetric methylene stretch exhibits a substantial SFG activity. Two possible reasons could lead to the loss of the central symmetry. Fluorination of the alkyl chain tail should induce charge redistribution along the C–C bond between adjacent CF_2 and CH_2 groups; as a result the two carbon atoms in the C_2H_4 unit would no longer be equivalent. A much higher hydrolysis rate of the

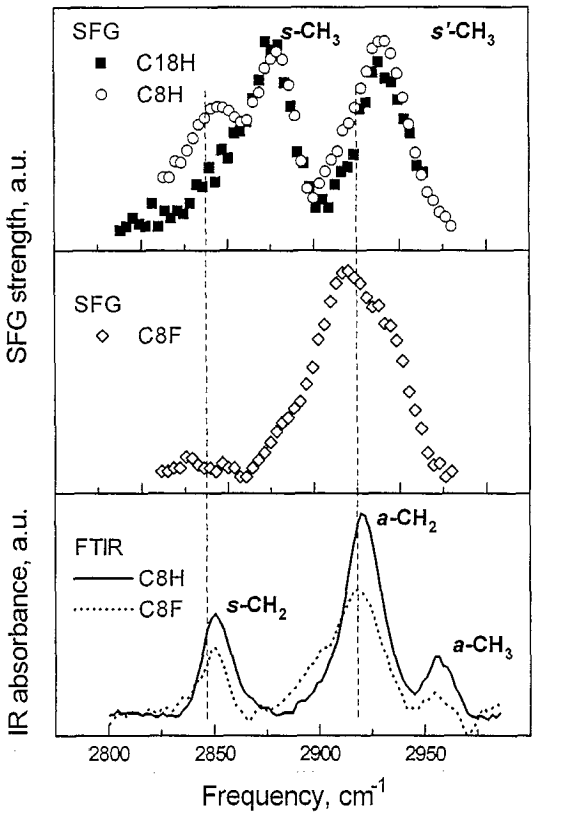

Fig. 2. Top: SFG spectra of C18H (OTS) and C8H monolayers. Middle: SFG spectrum of the C8F monolayer. Bottom: FTIR transmission\tqabsorption spectra of C8H and C8F monolayers.

silane head group in the fluorinated octyltrichlorosilane indicates that the fluorination of the alkyl chain tail influences the head group properties. Thus the non-fluorinated part of the chain located in between is unlikely to remain unaffected anyway. The other reason for disappearance of the central symmetry could be the twist of C_2H_4 unit, induced by the helical fluorinated part of the chain. In essence, any imaginable perturbation affecting only one side of the C_2H_4 unit would immediately lead to the loss of the central symmetry. However, the sole fact of a symmetry loss is not enough to explain the preferential enhancement of the antisymmetric CH_2 stretch in SFG. A rigorous calculation of the C8F vibrational spectrum is required.

While the SFG spectra of the C8F and C8H films are markedly different, their IR spectra plotted in Fig. 2 are fairly similar. Two major peaks correspond to the symmetric and antisymmetric CH_2 stretching modes. The methyl antisymmetric mode also clearly shows up in the C8H film spectrum. This spectrum is also very similar to the one of an OTS monolayer recorded by Ge et al. [8]. Despite the fact that only two from seven CH_2 groups are left in the C8F chain, the intensity of the methylene modes in its spectrum is only about 60% of that in the C8H. Some feature with the intensity almost at the noise level is present at the antisymmetric methyl stretching frequency. These two facts indicate that a hydrocarbon residue may contribute to the spectrum. If, in accord with XPS observations, the amount of the residue is around five methylene groups per C8F molecule, the resulting methylene absorption in the C8F film should be 54% compared to the C8H film. This number is in good agreement with the observed value of 60%.

SFG spectroscopy, contrary to FTIR, appears to be capable of distinguishing between C18H, C8H and C8F monolayers by their spectral features in the C–H stretching region. A loss of the central symmetry of the alkyl chain is easily detected by the appearance of new peaks in the SFG spectrum. A loss of the *trans*-configuration and the chain tail fluorination induce clearly different changes in the SFG spectrum, with symmetric methylene stretch dominating in the former case and antisymmetric stretch dominating in the latter case.

SFG spectra of various mixed monolayer samples are presented in the Fig. 3. In accord with the XPS data, it is seen that the spectral features continuously change from those characteristic for C8H to those of C8F with the increase of the fluorine content in the deposition solution. The fluorinated compound is indeed preferentially adsorbed, and the layer deposited with just 40% of it produces an SFG spectrum practically indistinguishable from the spectrum of the pure C8F.

It is also seen from the SFG spectra that adding just 11% (1:8) of the fluorinated alkylsilane into the solution leads to almost complete quenching of the methylene stretches at 2945 and 2920 cm^{-1} while the methyl stretches, characteristic for non-fluorinated alkylsiloxane film, still dominate in

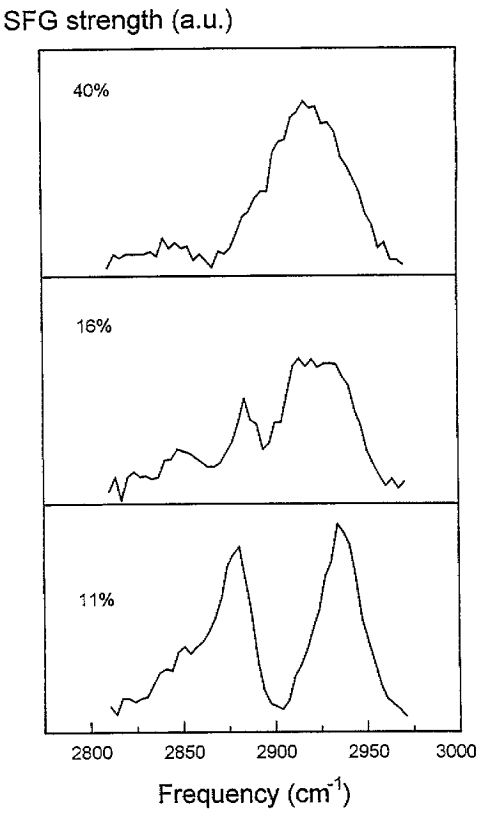

Fig. 3. Evolution of mixed monolayers SFG spectra with increasing (from bottom to top) fluorinated compound content in the deposition solution.

the spectrum. It seems that a relatively small amount of more rigid fluorinated alkyl chains incorporated in the film significantly decreases the defects concentration in non-fluorinated chains. For such influence to be possible, both C8H and C8F molecules must be closely coadsorbed. Thus we conclude that in contrast to the comparable LB film [8], which was found to consist of two separate phases, in our case a monolayer mixed to the molecular level is produced. Such a difference results most likely from the restricted surface mobility of the alkylsilanes during self-assembly; the molecules are chemisorbed shortly after reaching the surface before the process of phase segregation is finished.

For the mixed films with the fluorine content higher than in the 1:8 sample, the antisymmetric methylene stretch originates predominantly from the C8F because the response from methylene in the C8H is suppressed due to the improved ordering of the film. Thus the relative amplitude of antisymmetric methylene stretch peak can serve as a rough measure of the fluorine content in a mixed film with the pure C8F film as a reference. The amount of C8F in the 1:5 sample calculated this way is 56%, which is in reasonably good agreement with the XPS data (68%). A higher accuracy can be achieved by the deconvolution of all spectra into the single mode components, with subsequent fitting of the mixed film spectrum with the linear

combination of pure C8H and C8F. Assuming a purely homogeneous broadening (Lorentzian lineshape) we have obtained a value of 67 ± 5% for C8F content in the 1:5 sample, which coincides with the one derived from the XPS within the experimental error.

4. Conclusions

We have successfully performed deposition of the mixed fluorinated/non-fluorinated alkylsiloxane films on fused silica substrate by self-assembly. A continuously tunable mixed film composition was achieved. Different species are found to be closely coadsorbed on the surface and influence each other. In particular, relatively small amounts of fluorinated species incorporated into a non-fluorinated layer can significantly decrease the concentration of alkyl chain defects. The close coadsorption also indicates that different species have a limited surface mobility during self-assembly. Comparison of the XPS and SFG data shows that SFG spectroscopy of C–H stretching region can be used to estimate the relative concentrations of the species on the surface. Furthermore, SFG spectroscopy is shown to be capable of revealing the defects and symmetry perturbations in the alkyl chains of SAMs. These defects are not revealed by ordinary IR spectroscopy. The fluorinated alkylsilane demonstrated significantly higher surface affinity than its non-fluorinated analog under the same deposition conditions. All samples were found to contain a substantial amounts of hydrocarbon residue.

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