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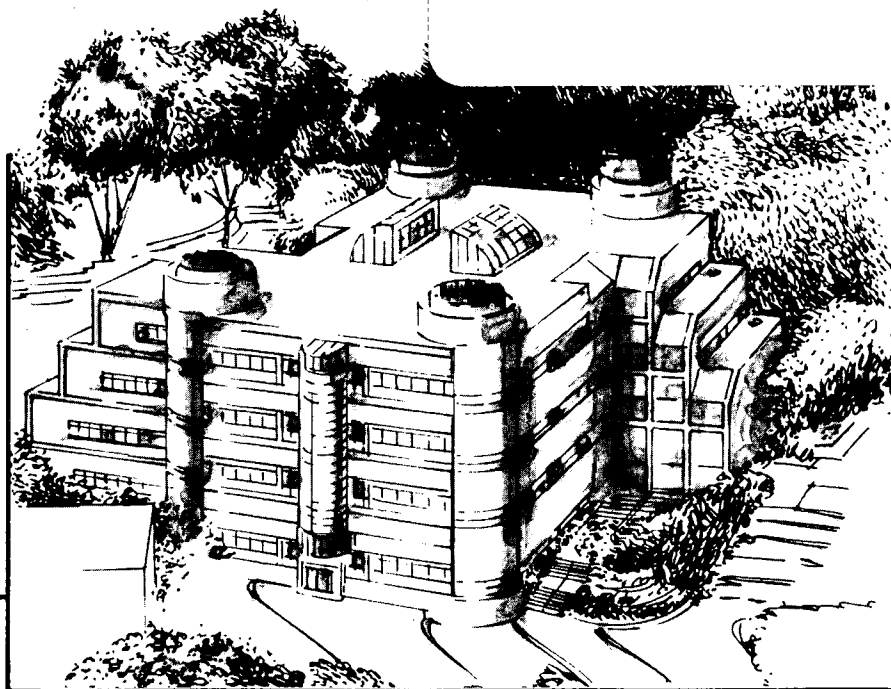1987-11-01

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VIBRATIONAL SPECTROSCOPY OF A SILANE MONOLAYER AT AIR/SOLID AND
LIQUID/SOLID INTERFACES USING SUM-FREQUENCY GENERATION

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ABSTRACT

We present the first application of infrared-visible sum-frequency generation to studies of liquid/solid interfaces. The spectra in the CH stretch region of a saturated monolayer of octadecyltrichlorosilane (OTS) adsorbed at various interfaces bound by a fused silica substrate were measured and compared. In every case, it was found that the OTS molecules were oriented with the alkane chains normal to the surface. The adsorption of OTS on silica from a solution was also monitored in-situ in real time.

The understanding of liquid/solid interfaces is of central importance in surface science and technology. For decades, they have been studied by methods such as contact angle measurements, capacitance measurements, and liquid chromatography, yielding mostly information on the macroscopic level. Techniques so successful at probing vacuum/solid interfaces are generally inapplicable here. The recently developed optical second harmonic generation (SHG) technique does allow one to probe various types of interfaces, including liquid/solid[1] and liquid/liquid,[2] but it is incapable of a selective study of adsorbed molecules via their vibrational spectroscopy. As a remedy, our group recently extended SHG to infrared-visible sum-frequency generation (SFG) for surface vibration spectroscopic studies.[3,4] In this paper, we report the first application of SFG to a liquid/solid interface. Although infrared techniques have been applied to probe the liquid/solid interface, SFG, being intrinsically surface sensitive, will allow the study of a much wider range of geometries and substrates.

The system we chose to study is octadecyltrichlorosilane (OTS) adsorbed at the interfaces between fused silica and different solvents. This is relevant to the recently developed reverse-phase liquid chromatography involving hydrocarbons bonded to silica particles immersed in a solvent.[5] The exact nature of the bonded molecular layer has attracted much theoretical and experimental interest.[6,7] Unfortunately, the investigations are generally impeded by the poorly characterized surface of the silica particles and the lack of sensitivity of the probes. We realized that SFG is an excellent tool for this problem since it can be applied to flat silica surfaces, allowing a better characterization of the bonded molecular layer.

Analogous to SHG, SFG is a second-order process and therefore is highly surface-specific. The surface nonlinear susceptibility responsible for the surface SFG can be written as

$$\chi_S^{(2)} = \chi_{NR}^{(2)} + \chi_R^{(2)},$$

where $\chi_{NR}^{(2)}$ is the nonresonant part and $\chi_R^{(2)}$ is the resonant contribution from the adsorbed molecules. With the local field correction neglected, $\chi_R^{(2)}$ is related to the resonant nonlinear polarizability $\alpha_R^{(2)}$ as

$$\left(\chi_R^{(2)}\right)_{\ell mn} = N_S \sum_{i,j,k} \left(\alpha_R^{(2)}\right)_{i,j,k} \langle\hat{\ell} \cdot \hat{i}\rangle\langle\hat{m} \cdot \hat{j}\rangle\langle\hat{n} \cdot \hat{k}\rangle,$$

where N_S is the surface molecular density, and the angular brackets around the products of unit vectors denote an average over molecular orientations. It can be shown from the microscopic expressions that[8]

$$\left|\alpha_{R,\ell mn}^{(2)}(\omega_{SF} = \omega_V + \omega_{IR})\right| \propto \left|\alpha_{R,nn}^{(1)}(\omega_{IR})\right|^{1/2} \left|\alpha_{R,\ell m\ell m}^{(3)}[\omega_{SF} = \omega_V + (\omega_{SF} - \omega_V)]\right|^{1/2},$$

$\alpha_R^{(1)}$ and $\alpha_R^{(3)}$ being the resonant linear and Raman susceptibilities of the adsorbed molecules, respectively. Measuring the components of $\chi_R^{(2)}$ allows then to determine the average orientation of the corresponding resonant mode.[8] For an in-plane isotropic surface, the nonvanishing elements of $\chi^{(2)}$ are

$$\chi_{zzz}^{(2)} \; ; \; \chi_{xxz}^{(2)} = \chi_{yyz}^{(2)} \; ; \; \chi_{xzx}^{(2)} = \chi_{yzy}^{(2)} \; ; \; \chi_{zxx}^{(2)} = \chi_{zyy}^{(2)} \; ,$$

with $\hat{z}$ chosen to be along the surface normal. When both ω_{SF} and ω_V are far away from resonance, we have the additional relation $\chi^{(2)}_{xzx} = \chi^{(2)}_{zxx}$.

The experimental setup has already been described in previous publications.[4,8] In the present experiment, the input pulses at 0.532 μm and at ~ 3.5 μm (tunable) had a pulsewidth of ~ 20 psec, a repetition rate of 10 Hz, and energies 1 and 0.2 mJ, respectively. The two beams were focused on the sample surface to a common area of ~ 0.1 mm^2, at incidence angles of 52° and 58° (in air), respectively. The IR pulse had a linewidth of ~ 6 cm^{-1}. Its frequency was calibrated to ± 1.5 cm^{-1} using the methane absorption spectrum. To calibrate and normalize the SF signal, SFG from a quartz crystalline plate was used.

OTS monolayers on fused silica substrates were prepared following the dipping method of Sagiv.[9] Surface coverage of $\gtrsim$ 20 Å^2/molecule are generally obtained.[10] This is significantly more closely packed than that of 60-100 Å^2/molecule usually achieved on silica gel particles in liquid chromatography.[7]

Let us first consider the importance of the bulk contribution to SFG from a liquid/solid interface. One might suspect that the resonant structure in the SFG spectrum could arise from solvent resonances. It could be due to either the anomalous dispersion of the refractive index around resonances affecting the Fresnel factors for SFG or the electric-quadrupole-type bulk nonlinearity. For the former, our calculations show only a 4% change to the SFG spectrum assuming that the solvent has an absorption line with a 20-cm^{-1} linewidth and a 10^3-cm^{-1} maximum absorption coefficient. It can therefore be neglected with our present experimental accuracy. The contribution from the bulk nonlinearity can be shown experimentally to be negligible through a

comparison of the observed SFG spectra of the OTS monolayer at fused silica/CCl_4 and fused silica/hexadecane interfaces. Both solvents only weakly interact with OTS, but hexadecane has strong IR absorption lines in the CH stretch region that we probed. Yet as shown in Fig. 1, the two spectra are essentially identical. This result is a striking demonstration of the surface specificity of the SFG spectroscopy.

We now discuss the OTS monolayer spectra in more detail. Let us first examine the spectra obtained from OTS adsorbed at the air/fused silica interface presented in Fig. 2 for three different polarization combinations. Three peaks are clearly present, all of which can be assigned to the CH stretches of the terminal CH_3 group: Those at 2878 and 2964 cm^{-1} arise from the symmetric (s) and asymmetric (d) stretches,[11,12] respectively, and the one at 2942 cm^{-1} presumably comes from the Fermi resonance between the s-stretch and the overtone of the CH bending mode.[13] The splitting of the two degenerate asymmetric stretches, d_x and d_y, cannot be resolved. Peaks for the CH_2 stretches (for example, s-stretch at 2850 cm^{-1}) are absent. These spectra closely resemble those observed for pentadecanoic acid (PDA) monolayers on the water surface.[8] They indicate that the OTS molecules have their long alkane chains straightened and aligned normal to the surface of the substrate. This conclusion agrees with the result derived from earlier work on saturated OTS monolayers on flat surfaces,[10] but is at variance with some of the model for hydrocarbons adsorbed on silica gel particles in chromatography.

The spectra in Fig. 2 can be analyzed quantitatively by modeling each resonant mode contributing to the spectra as a Lorentzian line convoluted with a Gaussian laser linewidth of 6 cm^{-1}. For the

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unresolved d_x and d_y stretches, we assumed that the two peaks were separated by 8 cm^{-1} as in the bulk alkane case. A consistent set of peak positions and widths could actually be obtained by fitting the three spectra this way. The results are summarized in Table I. The CH_3 s-stretch was most accurately determined, and was used to determine the average orientation of the CH_3 group.

As in the PDA case,[8] by taking the ratio of the s-stretch intensities of the (s-vis, p-IR) and (p-vis, s-IR) polarization combinations, we found that the CH_3 group has a tilt angle 50° < θ < 40° with respect to the surface normal, which is consistent with a chain inclined at no more than 15° from the surface normal. The apparently larger tilt than in the case of PDA on water could be due to the fact that the silica surface is relatively rough.

We now look at the spectra of OTS monolayers at CCl_4/fused silica and methanol/fused silica interfaces, shown in Fig. 3. For the CCl_4 case, the spectra are fairly similar to those in Fig. 2 for the air/solid interface. The difference in the two spectra of the (p-vis, p-IR) polarization combination is due to the fact that several $\chi^{(2)}$ components contribute to SFG with different Fresnel factors in this case. The spectra of Fig. 3(a) can be described by using the same "apparent" oscillator strength for the peaks as in the solid-OTS-air case with some adjustments in the peak positions and width (see Table I). Only the d-stretch peak broadened in a detectable way. The s-stretch remained essentially unchanged. This indicates that the orientation of the terminal methyl group and the chain conformation are not significantly different in the two cases. The peak positions in the CCl_4/OTS/silica spectra are red-shifted in comparison with those in

the air/OTS/silica spectra, in better agreement with the bulk frequencies. Similar shifts have been observed on Langmuir-Blodgett films where the d-stretch frequency appeared to be red-shifted by 6 cm^{-1} in changing from a monolayer to the multilayer system.[14] This is probably due to the interaction of the terminal methyl group with the environment. The local field effects might also account for part of this shift.

We now discuss the spectra of OTS at the methanol/silica interface [Fig. 3(b)]. Previous work using Fourier transform IR spectroscopy on OTS adsorbed on silica gel particles in deuterated methanol suggested a slight chain straightening of the silane upon adsorption of methanol.[15] Our spectra in Fig. 3(b) compared to the spectra in Fig. 3(a) with CCl$_4$ as the solvent indeed show an additional resonance at 2832 cm^{-1} (see Table I) which is close to the methanol s-stretch resonance (2834 cm^{-1}) in the liquid phase.[11] Since no signal should be expected from the bulk methanol suggested by the experiment with bulk hexadecane mentioned earlier, we attribute this resonance to the methanol adsorbate. The increase in the strength of the OTS methyl s-stretch in the spectrum with methanol as compared to the CCl$_4$ case can be accurately accounted by the increase of the Fresnel factor. This indicates that the adsorption of the methanol molecule has only a weak effect on the OTS orientation. Changes of the spectra in the 2950 cm^{-1} range arise because methanol has a strong Raman and IR active mode at 2946 cm^{-1}.[11] The contribution of methanol to the SFG spectra indicates that the monolayer has some polar ordering. In principle, a detailed determination of the polarization and optical phase of the molecular contribution should give the orientation of the methanol

adsorbates. We, however, did not attempt such a measurement here.

Comparing spectra of OTS at three different liquid/silica interfaces, we can conclude that the OTS monolayer configuration is hardly sensitive to the environment. This is surprising in view of the widely accepted belief in the chromatography field that solvents should have a swelling or shrinking effect on the monolayer. As already mentioned, there is a vast difference in the packing of the monolayer in our case (~ 20 $Å^2$/mol) and those usually achieved in liquid chromatography system (60-100 $Å^2$/mol). At higher surface densities, the intermolecular forces could supersede the action of the solvent. As the surface density is lowered, the molecule-substrate and the molecule-solvent interactions become more important leading to a richer variety of the monolayer configuration. Thus, SFG study of this system at lower surface densities could yield helpful information.

We have also used SFG to probe in-situ and in real time the adsorption of OTS at a liquid/silica interface. Although isotherms of the adsorption of OTS and other silanes have been reported,[10] to our knowledge, no in-situ probing of the adsorption has ever been performed due to the lack of an appropriate surface technique. To monitor the time-dependent adsorption of OTS by SFG, we set the IR pump frequency at the peak of the d-stretch resonance. Initially, a fresh solution of hexadecane, carbon tetrachloride and chloroform (80:12:8) filled the cell. At time t ~ 0, a similar solution containing .1% OTS started to flow through the cell. Figure 4 shows the SFG signal from the interface as a function of time with an integration time of 25s. The adsorption was nearly complete after 10 mn, in agreement with observations made ex-situ.[8] To fit the adsorption curve, we assume

simple Langmuir kinetics so that the surface nonlinearity takes the time dependent form $\chi_0 + \chi_{OTS}(1 - e^{-t/\tau})$, where χ_0 is the nonresonant interface nonlinearity in the absence of OTS, χ_{OTS} is the nonlinearity of the saturated OTS monolayer, and τ is the adsorption time constant. For the fit, we chose the following parameters: $\chi_0 = .65$, $\chi_{OTS} = -2.5 + i2.1$ and $\tau = 70s$. As seen in Fig. 4, with a proper choice of the $t = 0$ point, which is somewhat arbitrary because of the experimental uncertainty, the theoretical curve describes the data fairly well.

In conclusion, we have used SFG as a surface vibrational spectroscopic tool to study a silane monolayer at the air/silica and liquid/silica interfaces for various liquids. The spectra indicate that in all cases, the OTS molecules are oriented with their alkane chains essentially normal to the surface. Little difference was seen between polar and nonpolar liquids, although in the methanol case, the methanol molecules also appeared to adsorb at the interface. Our result is at variance with the picture assumed in liquid chromatography, but the difference could be understood from the different surface densities. We were also able to monitor in-situ the adsorption of OTS on fused silica in real time. This work demonstrates clearly the enormous potential of surface SFG for studies of liquid/ solid interfaces. It is therefore expected that the technique will find applications in many areas of surface science.

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Table I. Frequencies and linewidths of the methyl contributions to the spectrum.

	Silica-OTS-Air	Silica-OTS-Methanol	Silica-OTS-CCℓ₄
OTS.d_x-stretch	2969 (9)	2964 (13)	2964 (13)
OTS.d_y-stretch	2958 (9)	2952 (13)	2952 (13)
OTS.s-stretch + Fermi resonance	2942 (9)	2937 (9)	2937 (9)
OTS.s-stretch	2878 (7)	2875 (7)	2875 (7)
Methanol s-stretch		2832 (12)	

- Peak maxima $\pm$ 1.5 cm^{-1} on the frequency.

- Linewidths (in parenthesis), deconvoluted with a 6 cm^{-1} IR laser linewidth, $\pm$ 1 cm^{-1} accuracy.

Figure Captions

Fig. 1 SFG spectra at different interfaces in the (p_{vis}, p_{IR})

polarization combination. Dashes: silica-hexadecane

interface. Solid squares: silica-OTS-CCℓ_4 interfaces.

Triangles: silica-OTS-hexadecane interface. The dashed and

solid lines are guides for the eye.

Fig. 2 SFG spectra at the silica-OTS-air interface for various

polarization combinations: 1) (p_{vis}, p_{IR}); 2) (p_{vis}, s_{IR}); 3)

(s_{vis}, p_{IR}). The solid lines are guides for the eye.

Fig. 3 SFG spetra at (a) the silica-OTS-CCℓ_4 interface and (b) the

silica-OTS-methanol interface with the same polarization

combinations as in Fig. 2. The arrows indicate the methyl

s-stretch resonance of adsorbed methanol molecules.

Fig. 4 Adsorption of OTS at the fused silica/hexadecane-CCℓ_4-

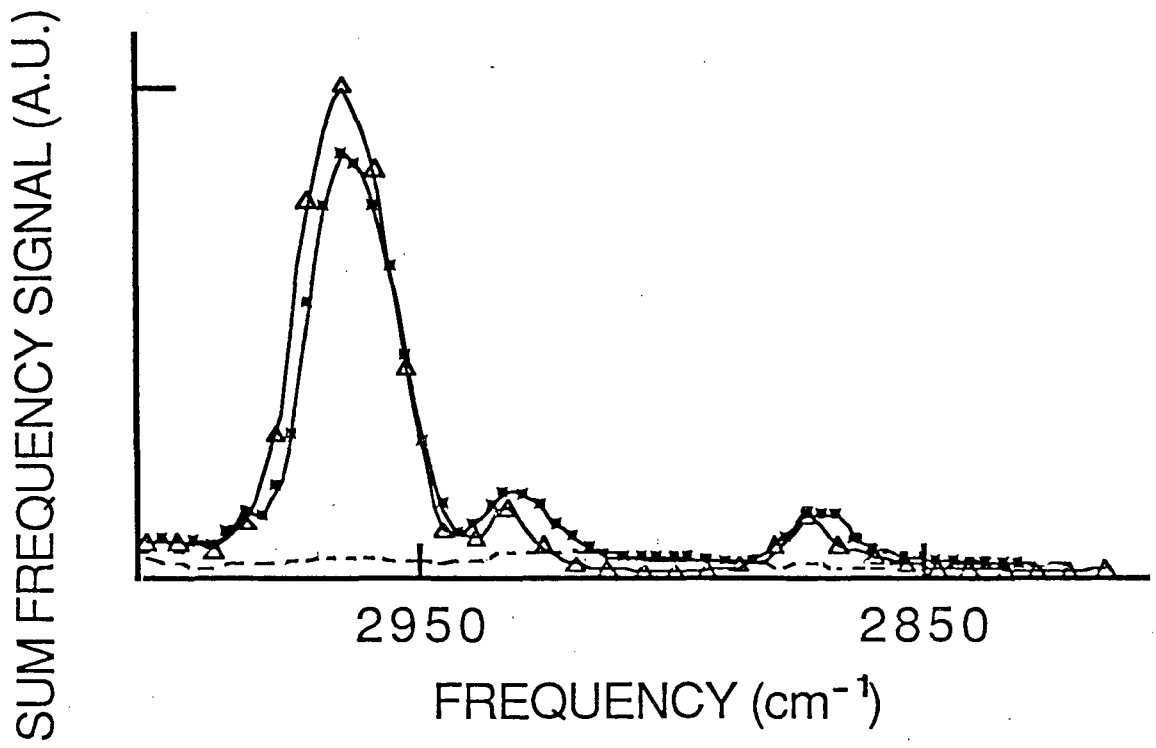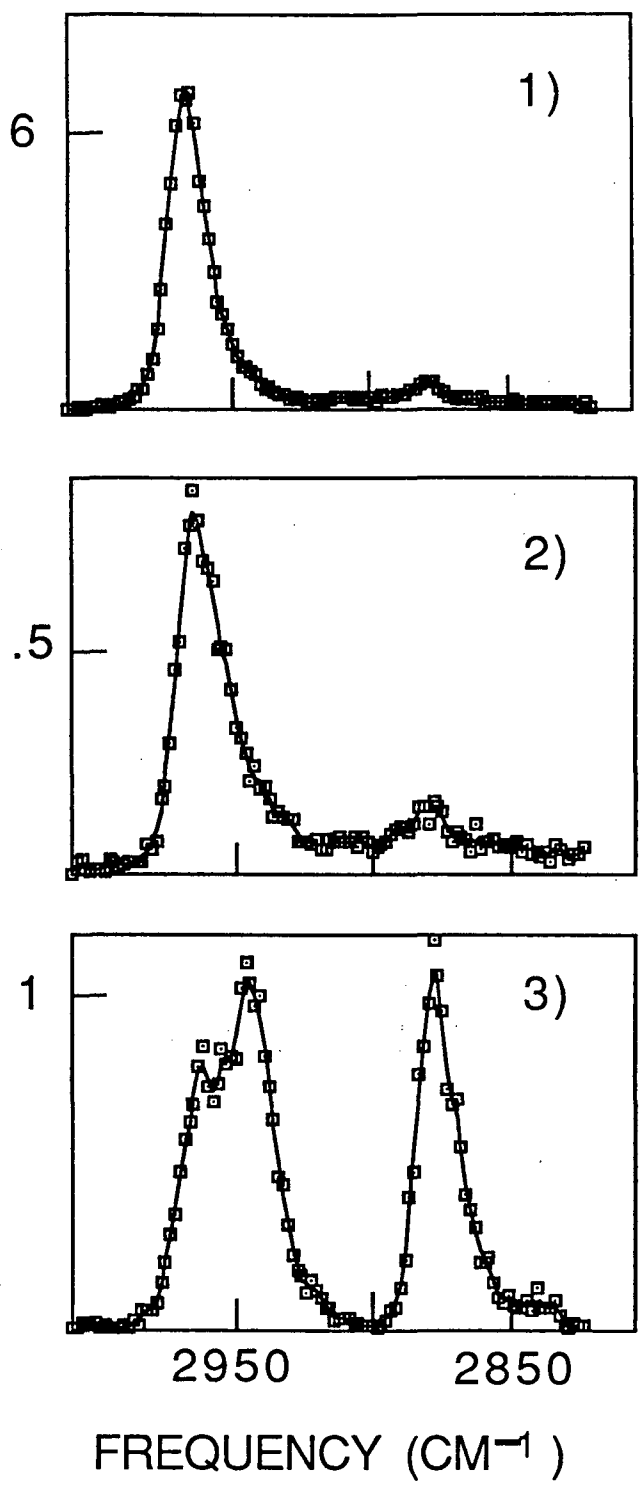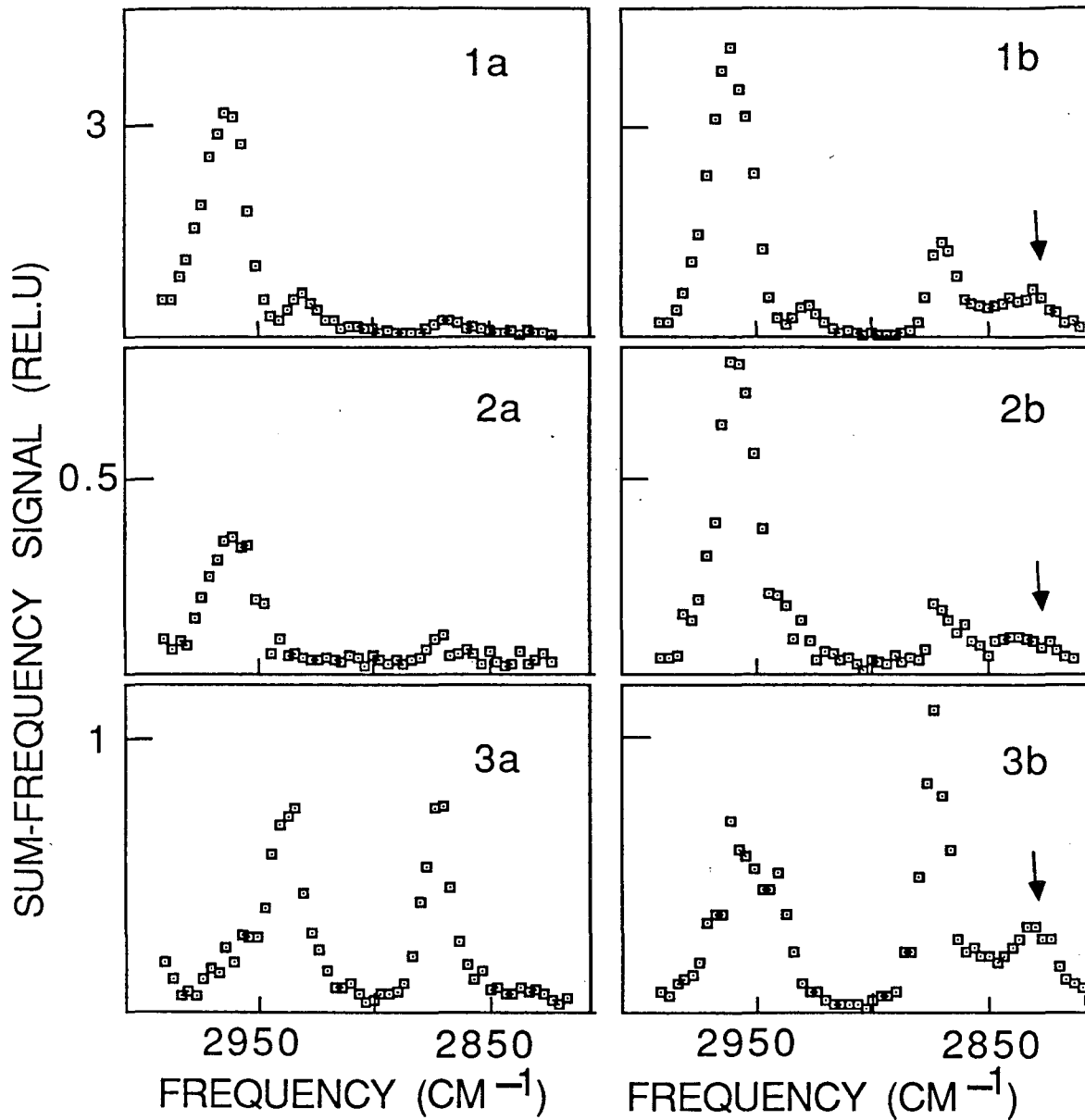chloroform interface as a function of time monitored by SFG.

Fig. 1
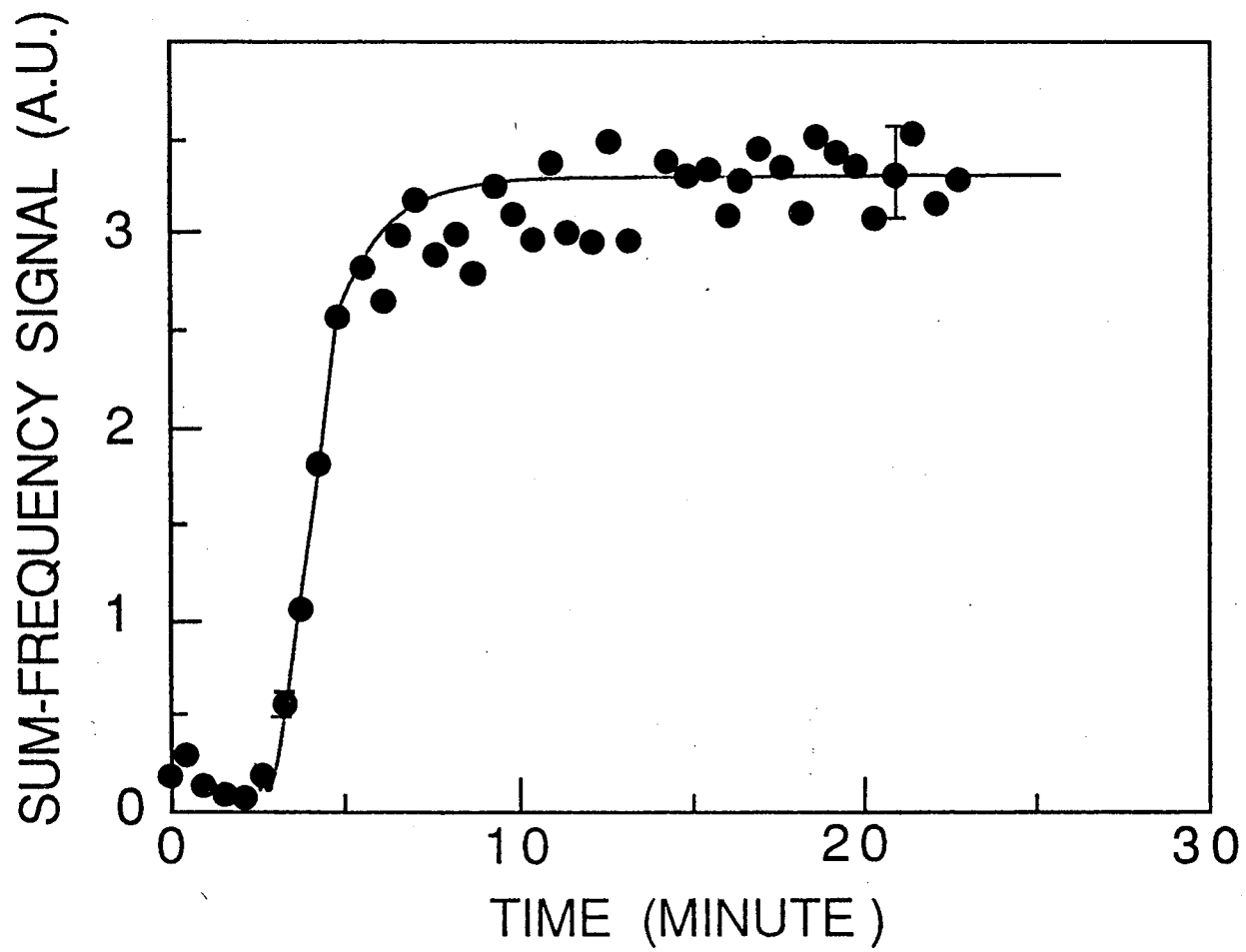
Fig. 2

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Fig. 3

Fig. 4

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