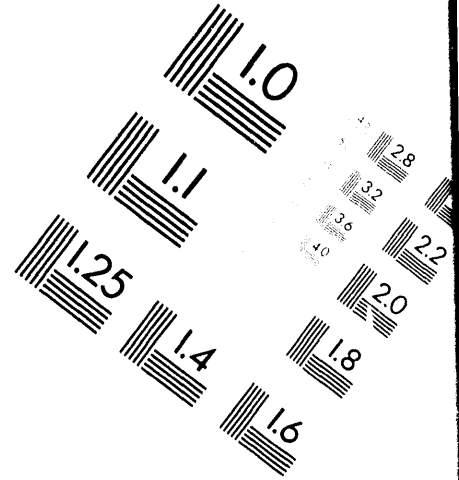
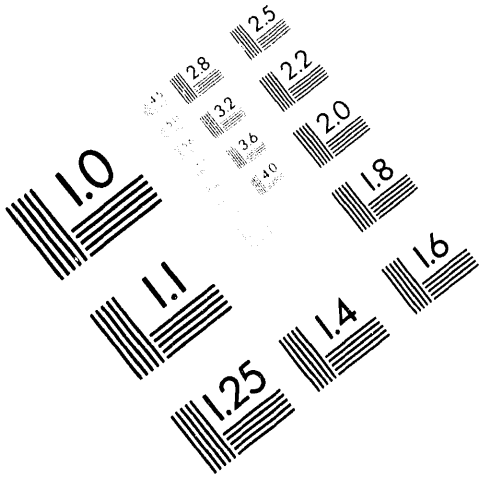




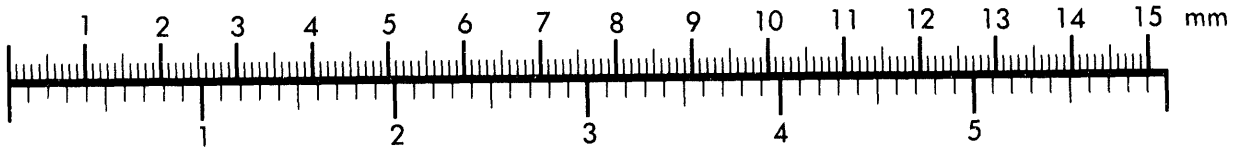
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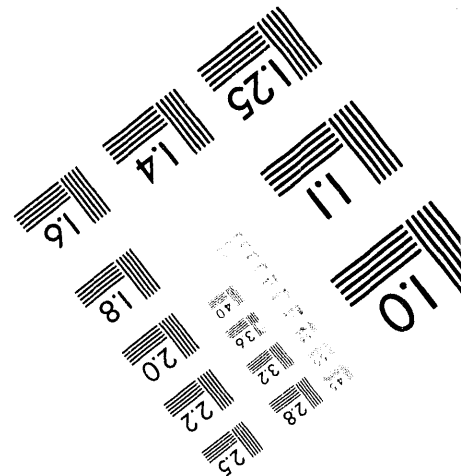
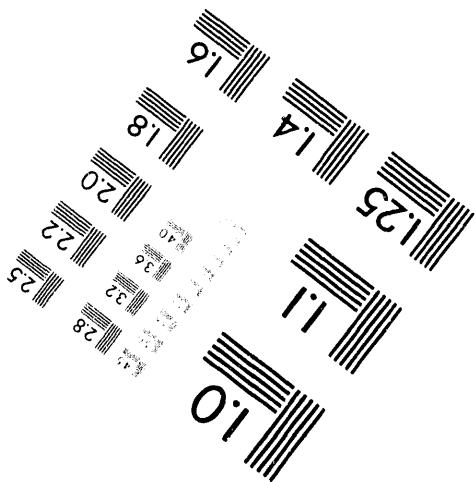
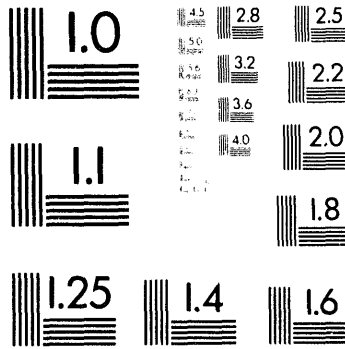
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# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials Sciences Division

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### Laser Probing of Interfaces

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March 1994



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## Laser Probing of Interfaces

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In the past decade, the possibility of using lasers to probe surfaces and interfaces has attracted a great of attention. Such techniques have the advantages of being able to interrogate a surface or interface in a non-detrimental and remote sensing way. Optical second harmonic generation (SHG) and sum frequency generation (SFG) have turned out to be most effective and versatile.<sup>1</sup> By symmetry, these second-order nonlinear optical processes are forbidden (under the electric dipole approximation) in media with an inversion center. They can therefore be highly surface specific. They are also capable of probing with high spatial, temporal, and spectral resolutions, suitable for *in-situ* studies of surfaces in hostile environment, and applicable to all interfaces accessible by light. Indeed, they have been successful in finding applications to a large variety of surface and interfacial problems: probing adsorption and desorption of molecules from surfaces,<sup>2</sup> measuring average molecular orientation of adsorbates,<sup>3</sup> monitoring surface symmetry and surface phase transitions,<sup>4</sup> conducting surface microscopy<sup>5</sup> and surface spectroscopy,<sup>6</sup> and many others. Here, we discuss a few examples to illustrate the power of the techniques.

Let me begin by describing briefly a typical experimental setup, which is schematically shown in Fig. 1. For SHG, a signal input beam at frequency  $\omega$  is incident on the sample. For SFG, two input beams at  $\omega_1$  and  $\omega_2$  are used, and the sum-frequency output at  $\omega_1 + \omega_2$  is measured. With selected input/output polarization combinations, the output are usually detected in the reflected direction with a photon counting detection system. From the measurement, the corresponding surface nonlinear susceptibility elements are deduced, providing characteristic information about the interface. Normally pulsed lasers are used in the experiment in order to achieve a reasonable signal-to-noise ratio. Consider a 1-ps laser pulse with a pulse energy of 1 mJ focused to a  $0.1 \text{ cm}^2$  spot on an interface. It can be estimated<sup>1</sup> that for a surface susceptibility of  $X^{(2)} = 10^{-15}$  esu, the SH signal generated from a single molecular monolayer at the interface is  $\sim 4 \times 10^5$  photons per pulse. With a typical detection system, this signal could yield a signal-to-noise ratio exceeding  $10^7$ .

To illustrate the monolayer sensitivity of SHG and SFG, we first discuss how SHG can be used to monitor adsorption and desorption of oxygen on silicon.<sup>7</sup> Oxidation of silicon is known to be an important problem for silicon device technology. In-situ monitoring of the presence of oxygen on silicon could provide useful information about the oxidation process. Figure 2 depicts the SH response to the adsorption of oxygen on Si(111) as a function of oxygen exposure. The decrease in the signal with time can be understood as follows: A clean Si(111) surface is covered by dangling bonds, which are

highly nonlinear and contribute to a relatively large SH signal. With oxygen adsorbed and bonded to Si at the surface, the dangling bonds are gradually eliminated, and the SH signal decreases accordingly. The data can be fit by the simple Langmuir model for adsorption as denoted in Fig. 2. The adsorbed oxygen can be desorbed if the sample is heated to a sufficiently high temperature. In fact, this is a known common procedure for cleaning silicon surfaces. As seen in Fig. 3, oxygen desorption from a heated Si(111) surface can also be monitored by SHG.

As another example, we discuss how we can use SHG to study surface-induced bulk alignment of liquid crystals(LC).<sup>8</sup> This is a problem of great importance in LC device technology since the procedure is commonly adopted in the construction of almost all LC devices. Yet the physical mechanism responsible for the effect is not fully understood. For homogeneous alignment (molecules lying flat and preferably aligned along one direction in the surface plane), mechanical rubbing of polymer-coated surfaces is the surface treatment often used. There are two possible mechanisms for the surface-induced bulk alignment. One similar to molecular epitaxy is based on short-range surface-molecule and then molecule-molecule interactions to align the bulk.<sup>9</sup> The other assumes that mechanical rubbing creates grooves on the surface and the bulk alignment relies on minimization of long-range interaction (mainly elastic) between the surface and the bulk.<sup>10</sup> To see which mechanism dominates, we need to know how the first LC monolayer at the surface is aligned. The alignment is expected to be good if the molecular epitaxy mechanism is operative, but no so if the long-range mechanism is effective. Clearly such information can be obtained from SHG measurements on the LC monolayer at the surface.

To find out whether the surface LC monolayer is aligned or not, we measure the azimuthal dependence of SHG from reflection by rotating the sample about its surface normal. We use four different input/output polarization combinations (p-in/p-out, p-in/s-out, s-in/s-out, and s-in/s-out). We have studied 8CB (octyl-cyanobiphenyl) monolayers on MAP (methylaminopropyltrimethoxy silane) - coated surfaces. With or without mechanical rubbing of the surfaces, the SHG signal is independent of the sample rotation, indicating that the monolayer orientation is azimuthally isotropic. The rubbed MAP-coated surface does yield homogeneous bulk alignment along the rubbing direction. The results therefore suggest that the alignment in this case must come from the above-mentioned long-range surface-bulk interaction.

The measurement on an 8CB monolayer adsorbed on polyimide-coated surface gives very different results. As shown in Fig. 4, if the surface is unrubbed, the SHG signal is azimuthally isotropic, reflecting the azimuthal symmetry of the LC monolayer orientation. With rubbing, the data show a clear two-fold symmetry about the rubbing direction. Thus for the rubbed polyimide-coated surface, the surface-induced homogeneous bulk alignment must come mainly from the molecular epitaxy mechanism. It has been proposed that rubbing stretches the polymer chain, causing the first monolayer of LC to align along the chain, and then the alignment grows epitaxially into bulk.<sup>9</sup> Our result on polyimide-coated substrates agree well with this picture.

Finally, we discuss SFG as a surface vibrational spectroscopic tool.<sup>11</sup> Let  $\omega_1$  be in the infrared and tunable. If  $\omega_1$  is scanned over a surface vibrational resonance, the SF signal is expected to be resonantly enhanced, providing therefore the spectroscopic information. With  $\omega_2$  in the visible, the SF output is also in the visible and can be detected with a monolayer sensitivity using a photomultiplier. Here, we take vibrational spectroscopy of a free water surfaces as an example.<sup>12</sup> Fig. 5 shows the SFG spectrum of the OH stretch modes from the liquid/vapor interface of pure water. The broad feature between 3200 and 3500  $\text{cm}^{-1}$  is assigned to OH modes of water molecules of which both H atoms are bonded to neighboring molecules. The isolated peak at 3680  $\text{cm}^{-1}$  has been observed in infrared absorption measurements of water clusters<sup>13</sup> and is clearly identified as the H-unbonded OH mode of a water molecule whose other H is bonded to a neighboring molecule.

The 3680  $\text{cm}^{-1}$  peak in Fig. 5 is established as a surface feature by two observations. First, it lies well outside of the bulk absorption band. Second, as seen in Fig. 5, the peak changes dramatically upon modification of the surface by the deposition of a long chain alcohol monolayer. The latter observation is due to quenching of the unbonded OH of the pure water surface by the adsorption of alcohol. Furthermore, the sharpening of the spectrum in the bonded OH region between 3200 and 3500  $\text{cm}^{-1}$  indicates that the water layer underneath the alcohol monolayer has become more structured and ice-like. The existence of free OH bonds at the water liquid/vapor interface is in qualitative agreement with the recent molecular dynamics simulation.<sup>14</sup>

We have discussed in this article only a few examples of applications of SHG and SFG to studies of surfaces and interfaces. But let there be no misunderstanding, the techniques are certainly not limited to only these few areas. They have actually already found a tremendously wide range of applications in many disciplines, as have been described in many recent review articles.<sup>1</sup> New opportunities are still being opened with these techniques. There is no doubt that SHG and SFG have already been established as indispensable major tools for surface analysis.

## 2. ACKNOWLEDGMENTS

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Fig. 5 SFG spectra, with the ssp polarization combination, of the pure water/vapor interface (dashed line) and a water surface covered by an alcohol monolayer compressed to 10 mN/m (dotted line). The infrared absorption spectrum of ice (solid line) (from E. Whallhey and J. E. Bertie, *J. Chem. Phys.* **46**, 1264 (1967)) is also shown for comparison. (after Ref. 12.)

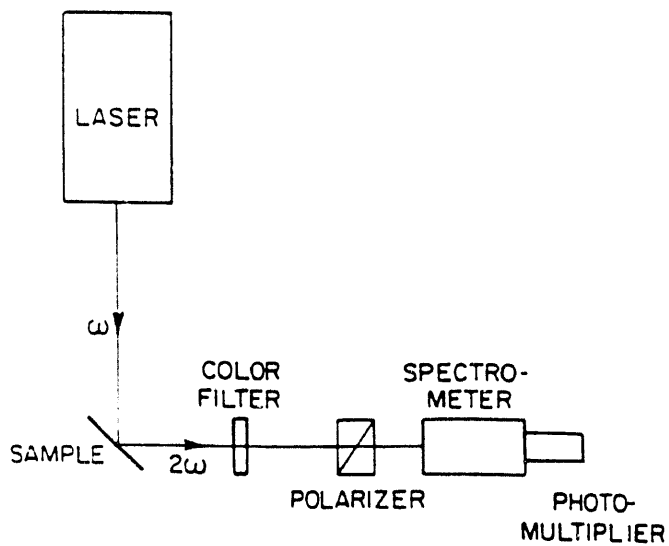


Fig. 1

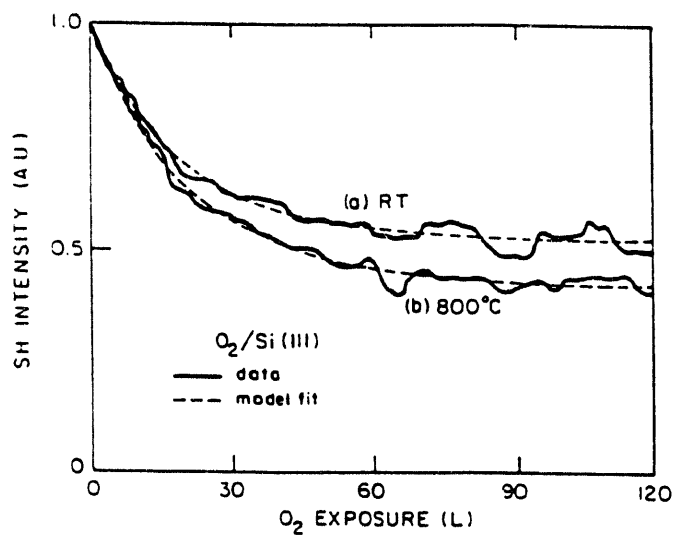


Fig. 2

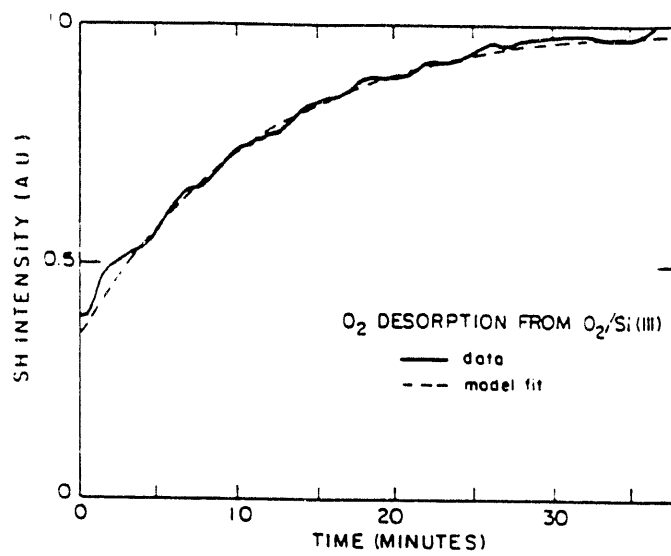


Fig. 3

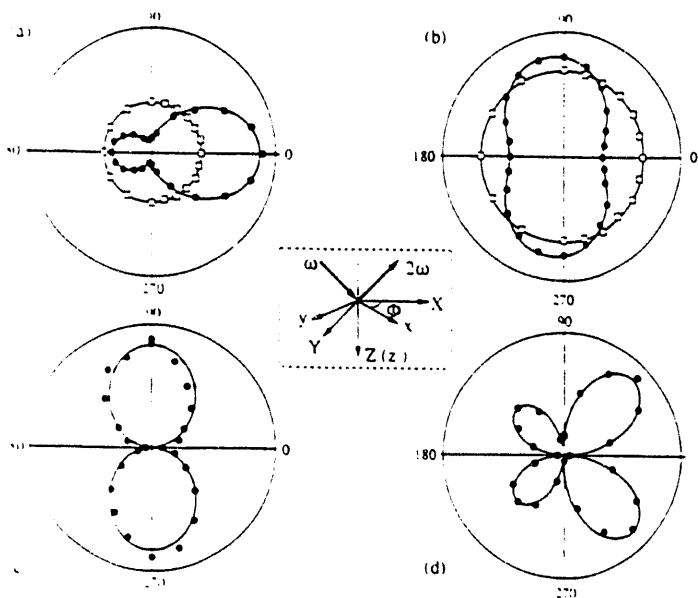


Fig. 4

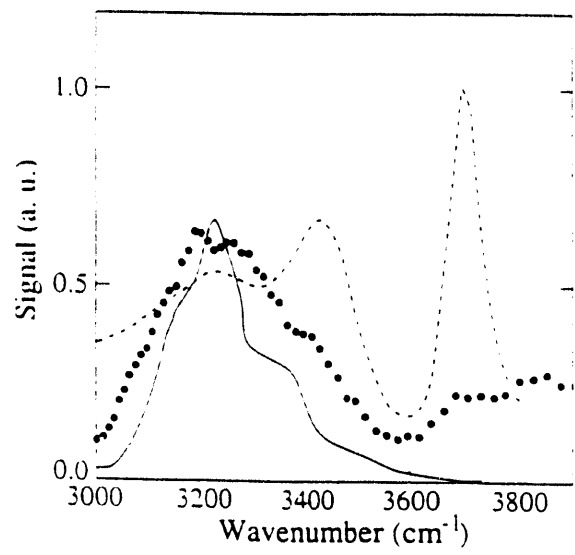


Fig. 5

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