γ

LBL--16406

DE84 001854

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Presented at the Sixth International Conference
on Laser Spectroscopy, Interlaken, Switzerland,
June 27 - July 1, 1983

RECENT STUDIES ON SECOND-HARMONIC GENERATION AS A SURFACE PROBE

H.W.K. Tom, T.F. Heinz, P. Ye, and Y.R. Shen

June 1983

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

Sixth International Conference
on Laser Spectroscopy,
June 27 - July 1, 1983
Interlaken, Switzerland

LBL-16406

Recent Studies on Second-Harmonic Generation as a Surface Probe

H. W. K. Tom, T. F. Heinz, Peixian Ye, and Y. R. Shen

Department of Physics
University of California
Berkeley, California 94720

and

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

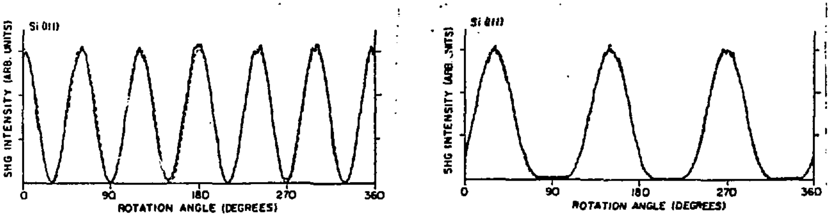
Optical second-harmonic generation (SHG) is forbidden in a medium with inversion symmetry, but is allowed at a surface or interface. The process is sensitive enough to respond to a submonolayer of surface atoms or molecules [1,2]. It can therefore be used as a means to probe surfaces or interfaces between two centrosymmetric media. The surface-specific nature of this purely optical method offers some unique advantages over the conventional surface probes. We have demonstrated in recent experiments that resonant SHG can allow us to obtain spectroscopic data of submonolayers of adsorbed molecules on a surface [3]. The signal was so strong that less than one tenth of a monolayer of dye molecules could be easily detected. The method can be applied to molecules adsorbed at an interface between two dense media such as a liquid/solid interface. Then, using SHG, adsorption isotherms of adsorbates on substrates can be measured [4].

In many applications of the technique, one is interested in how large the bulk contribution to SHG is in comparison with the surface contribution. Second-order nonlinear optical processes are forbidden in a medium with inversion symmetry only in the electric-dipole approximation. Could SHG from electric-quadrupole and magnetic-dipole contributions in the bulk be so strong as to mask out the electric-dipole contribution from the surface? In our studies of molecular adsorbates, we have found that the SH signal from a centrosymmetric substrate can be changed appreciably by the adsorption of a monolayer [5]. This clearly indicates that it is the adsorbate layer rather than the bulk of the substrate which dominates the SHG process. We are, however, also interested in developing the SHG technique for studying bare surfaces, and would like to know the relative bulk and surface contribution to SHG in such cases.

We have studied this problem experimentally by measuring the SHG from well-defined faces of a crystalline material. Consider the case in which a linearly polarized laser beam is incident on the surface of a silicon sample, and the SHG is measured as the sample is rotated about its surface normal. The induced nonlinear polarization at 2ω is expected to have two terms: an isotropic term which is independent of the sample rotation, and an anisotropic term which reflects the structural symmetry of the surface and the bulk. One can separate the two terms by measuring the s-polarized SH output for p-polarized pump input because the SH signal in this case comes from the anisotropic term only. It can be shown, by symmetry, that for the (100) face of Si, the anisotropic term arises solely from the bulk, while the isotropic term arises from both the bulk and the surface layer [6]. Consequently, by comparing the s-polarized to another polarized (say, p-polarized) SH signal for a p-polarized input laser beam, we can find the relative contributions of the bulk and the surface to the SHG from the given sample.

Our experimental results on Si (100) under laser excitation at 5320 Å showed that the s-polarized SH output was much weaker than the p-polarized output, but this difference was mainly due to the different radiation efficiencies in the two cases. Quantitative analysis of the experimental data allowed us to estimate the relative magnitudes of the isotropic part versus the bulk anisotropic part of the effective nonlinear susceptibilities. We found that they were of the same order of magnitude.

For the SHG from the Si (111) surface, the anisotropic term contains contributions from both the surface and the bulk. The surface anisotropic term should reflect the 3m symmetry of the surface structure. When the anisotropic term is isolated by the polarization conditions discussed above, the SH output, being proportional to the square of the nonlinear polarization, should exhibit a 6m symmetry. This is indeed what we observed, as shown in Fig. 1a. For other output polarizations, both the isotropic and the anisotropic parts contribute to the signal, so the output should show a 3m symmetry with 3 major peaks 120° apart and 3 minor peaks in between. When the incidence angle or polarization of the input laser beam is adjusted properly, the isotropic and anisotropic parts can be made of equal magnitude. Then, the three minor peaks reduce to zero and only the three major peaks should be present. As shown in Fig. 1b, this is also what we found experimentally for a p-polarized input beam incident at 45°. The results led to the conclusion that the anisotropic part of the surface nonlinear susceptibility was about 5 times weaker than the isotropic part.



(a) (b)

Fig. 1. SHG intensity for p-polarized pump radiation from a Si (111) surface vs. the angle of rotation about the surface normal: (a) For s-polarized SH output the signal is due solely to the anisotropic part of the nonlinear polarization. (b) For p-polarized SH output the isotropic and the maximum value of the anisotropic contributions to the nonlinear polarization are roughly equal [experiment ——; theory ---]

The above study suggests that although the surface and bulk contributions are equally important, the SHG from a surface can still be used to probe the structural symmetry of the surface layer, if it is sufficiently different from that of the bulk. In the case of molecular adsorbates, the SH signal from the adsorbate layer is expected to be at least comparable to that from the crystal surface layer, and can thus provide information about the symmetry of the molecular arrangement on the substrate. Indeed, using this technique, we have found that the azimuthal distribution of molecular adsorbates on fused quartz is most likely isotropic [3,5]. The polarization dependence of the surface-specific SHG also allows us to obtain information about the average orientation of molecular adsorbates on a substrate [5]. This follows from the fact that the nonlinear susceptibility $\overleftrightarrow{\chi}^{(2)}$ of the adsorbate layer is related to the nonlinear polarizability $\overleftrightarrow{\alpha}^{(2)}$ of the adsorbates by the geometric tensor $\langle T \rangle$ describing the average molecular orientation

$$\chi^{(2)}_{ijk} = \langle T^{\lambda\mu\nu}_{ijk} N\alpha^{(2)}_{\lambda\mu\nu}. \qquad (1)$$

Here, $T^{\lambda\mu\nu}_{ijk}$ represents the coordinate transformation between the molecular (ξ, η, ζ) system and the lab (x, y, z) system, and N is the surface density of the adsorbates. Measurements of $\chi^{(2)}_{ijk}$ or of the ratios of various components of $\overleftrightarrow{\chi}^{(2)}$ should therefore give us the average molecular orientation.

We have recently applied this technique to measure the molecular orientation of p-nitrobenzoic acid (PNBA) on fused quartz at both air/quartz and ethanol/quartz interfaces [5]. Taking the orientational distribution to be sharply peaked, the long axis of PNBA was found to be tilted from the surface normal by ~ 40° in the liquid and ~ 70° in the air. The difference could be explained by the solvation energy of PNBA in the liquid.

It should however be noted that the local-field effect has been neglected in Eq. (1). The local field on adsorbed molecules arises from the induced dipole-induced dipole interaction between molecules and the induced dipole-image dipole interaction between the molecules and the substrate. It can be decomposed into a spatially non-varying part and a spatially varying part [7]. The former can be described by the use of a local-field correction factor. The latter modifies the transition matrix elements in the molecular polarizabilities. Both components of the local field contribute to the effective nonlinear polarizability of the adsorbed molecules. Their effect can be estimated by a calculation using the classical point-dipole model. It is found that if the center of the main electronic cloud which contributes to the molecular polarizability is more than 2.5 A away from a substrate, the local-field effect from the induced dipole-image dipole interaction is negligible. If the molecules are sufficiently far apart (> 10 A), then the local-field effect due to molecule-molecule interaction is also negligible.

In our experiment with PNBA adsorbed on quartz, the classical point-dipole calculation shows that the local-field effect should be negligible. Our measured orientations of PNBA on quartz should therefore be acceptable. This conclusion is supported by the experimental fact that the measured orientations were independent of the laser frequencies used [5]. It is improbable that the orientations inferred from Eq. (1) should be frequency independent if the local-field effect were important, since the latter should be quite different for frequencies ranging from on-resonance to far off-resonance.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098. H.W.K.T. acknowledges a Hughes Fellowship; T.F.H. acknowledges an IBM fellowship.

1. J.M. Chen, J.R. Bower, C.S. Wang, and C.H. Lee, Opt. Comm. 9, 132 (1973).
2. C.K. Chen, T.F. Heinz, D. Ricard, and Y.R. Shen, Phys. Rev. Lett. 46, 1010 (1981).
3. T.F. Heinz, C.K. Chen, D. Ricard, and Y.R. Shen, Phys. Rev. Lett. 48, 478 (1982).
4. C.K. Chen, T.F. Heinz, D. Ricard, and Y.R. Shen, Chem. Phys. Lett. 83, 455 (1981).
5. T.F. Heinz, H.W.K. Tom, and Y.R. Shen, to be published.
6. H.W.K. Tom, T.F. Heinz, and Y.R. Shen, to be published.
7. Peixian Ye and Y.R. Shen, to be published.

DISCLAIMER