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Local and nonlocal surface nonlinearities for surface optical second-harmonic generation

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We investigate the physical origins of the surface nonlinear susceptibility responsible for surface optical second-harmonic generation. Experiments performed on simple covalent systems were designed to distinguish between the nonlocal electric-quadrupole-type nonlinearity induced by field discontinuity and the local intrinsic, electric-dipole-type nonlinearity of a surface or interface. We find that both mechanisms could operate: The latter usually dominates when the surface layer has a strong structural asymmetry with the fundamental or the second-harmonic frequency at resonance with a dipole-allowed transition.

I. INTRODUCTION

Optical second-harmonic generation (SHG) has been recently used as a surface probe to study a wide variety of surfaces and interfaces.[1] The technique is based on the principle that a second-order process is forbidden in a medium with inversion symmetry under the electric-dipole approximation, but is necessarily allowed at an interface. The SH signal generated in reflection from an interface between two centrosymmetric media partly comes from the interfacial layer with electric-dipole contribution and partly from the bulk with electric-quadrupole and magnetic-dipole contributions;[2–4] the former part often dominates or is at least comparable to the latter.[1] While it is easy to see that the strong surface nonlinearity arises from the broken symmetry at the interface, the more detailed physical origin of the surface nonlinearity is still a subject of confusion. Is the field discontinuity[5] or the structural discontinuity,[6] or both, at the interface responsible for the nonlinearity? Is the nonlinearity dominated by local or nonlocal response of the interfacial layer to the applied field?

In an important earlier work by Bloembergen *et al.*,[5] the electric-quadrupole (nonlocal) contribution to the surface nonlinearity resulting from the rapid variation of the normal component of the electric field across the interface was stressed. This led to the belief that surface SHG would be insensitive to molecular adsorbates on metal surfaces, and only weakly sensitive to adsorbates on low-refractive-index materials. On the other hand, recent experiments on better-characterized surfaces have shown that SHG can be a sensitive probe of the surface structure and molecular adsorbates on surfaces.[1] They indicate that the dipole (local) contribution to the surface nonlinearity in many cases may actually dominate.[6] Thus it is obvious that a better understanding of the physical origin of the surface nonlinearity is needed in order to further develop SHG as a surface-analytical technique.

While both of the above-mentioned contributions to the surface nonlinearity have been discussed separately in the literature, they have never been studied together in a unified, systematic way. In a recent publication,[7] we showed, by a rigorous derivation, that surface SHG can be characterized by an effective surface nonlinear susceptibility and the latter actually consists of a local electric-dipole term and a nonlocal electric-quadrupole and magnetic-dipole term. Which one may dominate would depend on the characteristics of the particular surface system in question. As this is important for basic understanding of surface SHG, an experimental verification of the theoretical analysis is clearly in order.

In this paper we report our recent experimental endeavors in sorting out the local and nonlocal contributions to the surface nonlinearity for surface SHG. According to theory, the local contribution depends only weakly on the dielectric constants of the adjacent media at the interface. The nonlocal contribution, on the other hand, is highly sensitive to the difference of the two dielectric constants, becoming vanishingly small when the two are matched. Thus, experimentally, the two contributions can be most easily sorted out by varying the dielectric constant of one of the media. In doing so, however, one must be sure that modification of the interfacial structure does not happen. In our experiment, therefore, a liquid—fused-silica interfacial system was studied, as it is then possible to choose various liquids with a range of different dielectric constants which are chemically nonreactive to fused quartz.

In Sec. II we first give a brief review of the underlying theory for surface SHG and the associated surface nonlinearity. The origins of the local and nonlocal contributions to the surface nonlinear susceptibility are identified and discussed in detail. We then present in Sec. III our experimental results which demonstrate that indeed both contributions to the surface nonlinearity exist and their relative strength is a characteristic of the system under investigation. The local contribution can be strongly enhanced when SHG is at resonance with an allowed transition involving a surface state, such as the excited state of an adsorbed molecule. Finally, in Sec. IV we discuss qualitatively the consequences of our findings on the applications of SHG to surface studies, in particular, to the probing of molecular adsorbates on different types of substrates and to the determination of orientation and distribution of the molecular adsorbates.

II. THEORETICAL BACKGROUND

In this section we shall briefly review the theoretical background of our problem at hand. The emphasis is on an explicit exposition of the physical origins of the surface optical nonlinearity.

Consider, for simplicity, an interface between two transparent, nonmagnetic, isotropic media 1 and 2. The interface is also assumed to have an in-plane isotropy. A fundamental beam at frequency ω in the x-z plane is incident on the interface ($z=0$) from medium 1 ($z<0$). The SH output in the reflected direction is generated by the nonlinear polarization induced both in the bulk and at the interface. The bulk, being centrosymmetric, has its nonlinearity coming from the electric-quadrupole and magnetic-dipole contributions. The general expression for the bulk nonlinear polarization is[5]

$$\begin{aligned}\mathbf{P}_i^{(2)}=&(\delta_i-\beta_i-2\gamma_i)[\mathbf{E}(\omega)\cdot\nabla]\mathbf{E}(\omega)\\&+\beta_i\mathbf{E}(\omega)[\nabla\cdot\mathbf{E}(\omega)]+\gamma_i\nabla[E^2(\omega)]\ ,\end{aligned} \tag{1}$$

where $i=1,2$ refers to the two adjacent media, and δ_i, β_i, and γ_i are constants. The surface nonlinear polarization induced at the interface, in the limit of an interface-layer thickness much smaller than the optical wavelength,[7] can be written as

$$\mathbf{P}_s^{(2)}(2\omega)=\overleftrightarrow{\chi}_s^{(2)}:\mathscr{E}(\omega,z=0)\mathscr{E}(\omega,z=0) \tag{2}$$

localized at $z=0$, where $\mathscr{E}_x\equiv E_x$, $\mathscr{E}_y\equiv E_y$, and $\mathscr{E}_z\equiv D_z$. Note that we have purposely defined the surface nonlinear polarization in terms of field components continuous across the interface, i.e., the tangential components of the electric field $\mathbf{E}$ and the normal component of the displacement current $\mathbf{D}$, in order to avoid confusion raised by the field variation across the interface layer.

Using $\mathbf{P}_i^{(2)}$ and $\mathbf{P}_s^{(2)}$ in Eqs. (1) and (2) as the source terms for SHG, we can then solve the Maxwell equations to find the SH output. We consider in this paper only the case where the fundamental input is linearly polarized with both s and p components and the SH output is s polarized, since in this case, the bulk contribution is strongly suppressed. The SH field radiated in the reflected direction is then found to be

$$\begin{aligned}E_y(2\omega)=&\,i(4\pi)\left[\frac{2\omega}{c}\right]^2\frac{1}{K_{1z}+K_{2z}}\left[2\chi_{s,yzy}^{(2)}+\frac{K_{2z}k_{2z}}{K_{1z}^2\epsilon_1\epsilon_2}(\epsilon_1-\epsilon_2)(\delta_1-\beta_1-2\gamma_1)\right]\\&\times\frac{\cos\theta_1}{\epsilon_1}\left[1+\frac{\tan(\theta_1-\theta_2)}{\tan(\theta_1+\theta_2)}\right]\left[1-\frac{\sin(\theta_1-\theta_2)}{\sin(\theta_1+\theta_2)}\right]E_s(\omega)E_p(\omega)\ ,\end{aligned} \tag{3}$$

where $\mathbf{k}_i$ and $\mathbf{K}_i$ are the fundamental and SH wave vectors in medium i, respectively, ϵ_i is the dielectric constant at ω in medium i, θ_1 and θ_2 are the angles of incidence and refraction of the fundamental beam, and $E_s(\omega)$ and $E_p(\omega)$ are the s and p components of the input field in medium 1. The bulk contribution here is given by the $(\delta_1-\beta_1-2\gamma_1)$ term. It arises only as a result of nonlinear interaction between the incoming and reflected fundamental waves in medium 1. In the low-frequency limit, it can be shown that $\delta_1-\beta_1-2\gamma_1$ should vanish.[5] Measurements of the SHG would then yield simply the surface nonlinearity characterized by $\chi_{s,yzy}^{(2)}$.

We now discuss in more detail how the surface susceptibility $\chi_s^{(2)}$ comes about. We realize that in reality the interface layer has a finite thickness on the microscopic scale. Both the material structure and the electromagnetic fields vary rapidly across this layer. The surface polarization of Eq. (2) is actually a quantity obtained from integration of the volume polarization across the layer

$$P_{sy}^{(2)}(2\omega)=\int_I P_y^{(2)}(2\omega,z)dz\ , \tag{4}$$

where I denotes the interface layer over which the integration extends. The volume polarization $P^{(2)}$ here is an effective polarization that includes all the multipole[2,3] terms. The multipole expansion of $P^{(2)}$ gives

$$\begin{aligned}\mathbf{P}^{(2)}(2\omega,z)&=\mathbf{P}^D(z)-\nabla\cdot\overleftrightarrow{Q}(z)+c\nabla\times\mathbf{M}(z)+\cdots\\&=\int\overleftrightarrow{\chi}^D(z,z',z''):\mathbf{E}(z')\mathbf{E}(z'')dz'dz''-\nabla\cdot\int\overleftrightarrow{\chi}^Q(z,z',z''):\mathbf{E}(z')\mathbf{E}(z'')dz'dz''\\&\quad+c\nabla\times\int\overleftrightarrow{\chi}^M(z,z',z''):\mathbf{E}(z')\mathbf{E}(z'')dz'dz''+\cdots\ ,\end{aligned} \tag{5}$$

where D, Q, and M denote the electric-dipole, electric-quadrupole, and magnetic-dipole terms, respectively. Since the susceptibilities $\overleftrightarrow{\chi}^\mu(z,z',z'')$ ($\mu=D,M,Q$) are response functions of the medium and are expected to be fairly local, they can be expanded into a power series

$$\begin{aligned}\chi^\mu(z,z',z'')=&\overleftrightarrow{\chi}^\mu(z)\delta(z'-z)\delta(z''-z)\\&+\overleftrightarrow{\chi}_A^\mu[\nabla\delta(z'-z)]\delta(z''-z)\\&+\overleftrightarrow{\chi}_B^\mu\delta(z'-z)[\nabla\delta(z''-z)]+\cdots\end{aligned} \tag{6}$$

and hence

$$\int \overleftrightarrow{\chi}^{\mu}(z,z',z''):\mathbf{E}(z')\mathbf{E}(z'')dz'dz'' = \overleftrightarrow{\chi}^{\mu}(z):\mathbf{E}(z)\mathbf{E}(z)+\overleftrightarrow{\chi}^{\mu}_{A}(z):[\nabla\mathbf{E}(z)]\mathbf{E}(z) + \overleftrightarrow{\chi}^{\mu}_{B}:\mathbf{E}(z)[\nabla\mathbf{E}(z)]+\cdots \quad . \tag{7}$$

Inserting Eq. (7) into Eq. (5) and then the expression of $P_y^{(2)}$ into Eq. (4) and comparing Eq. (4) with Eq. (2), we can show that

$$\chi^{(2)}_{s,yzy}D_z(z=0)E_Y(z=0) = \int_I \left[\chi^{D}_{yzy}E_z(z)-\frac{\partial}{\partial z}[\chi^{Q}_{zyzy}E_z(z)]E_y(z) + \chi^{D}_{A,yzzy}\left[\frac{\partial}{\partial z}E_z(z)\right]E_y(z)\right]dz \quad . \tag{8}$$

If we let $E_z(z)=s(z)D_z(z)$,[7] then since $D_z(z)$ is continuous across the interface, we find

$$\chi^{(2)}_{s,yzy}=\int_I \left\{ \chi^{D}_{yzy}(z)s(z)-\frac{\partial}{\partial z}[\chi^{Q}_{zyzy}(z)s(z)] + \chi^{D}_{A,yzzy}(z)\frac{\partial}{\partial z}s(z)\right\}dz \quad . \tag{9}$$

Notice that $s(z)=1/\epsilon_i$ ($i=1$ or 2) away from the interface so that $s(z)$ varies from $1/\epsilon_1$ to $1/\epsilon_2$ across the interface.

We can now identify the physical origins of the various terms in $\chi^{(2)}_{s,yzy}$ in Eq. (9). The first term in the integral is the electric-dipole term which is nonvanishing because the interface layer, different from the isotropic bulk, has a structure with no inversion symmetry. The second term actually leads to electric-quadrupole radiation at 2ω from the interface. This is a term that has so far been forgotten in the earlier papers on surface SHG. Its integration across the interface gives

$$-\int_I \frac{\partial}{\partial z}[\chi^{Q}_{zyzy}(z)s(z)]dz=\frac{\chi^{Q}_{zyzy}(0^-)}{\epsilon_1}-\frac{\chi^{Q}_{zyzy}(0^+)}{\epsilon_2} \quad , \tag{10}$$

which is often nonvanishing if there is a structural disparity between the two bounding media. The third term in the integral in Eq. (9) comes from the field discontinuity, i.e., the rapid field variation across the interface. This is usually regarded in the literature as the electric-quadrupole (nonlocal) contribution to the surface nonlinearity. If the dielectric constants of the two media are matched, then the field becomes continuous across the interface and this particular term should vanish.

From the above discussion, we can see that if we vary the dielectric constant ϵ_1 of medium 1, we expect the nonlocal contribution to the surface SHG due to the field discontinuity to vanish as $\epsilon_1 \rightarrow \epsilon_2$. The contribution described by Eq. (10) due to the structural disparity is also expected to reduce significantly. Only the electric-dipole contribution from the interface layer does not change very much with the variation of ϵ_1. This is the basis of our experimental test of the existence of different physical mechanisms for surface nonlinearity reported in Sec. III.

III. EXPERIMENTAL RESULTS AND DISCUSSION

We present in this section results of SHG experiments designed to illustrate the various physical mechanisms responsible for the surface nonlinearity. We chose to study SHG from liquid-solid interfaces. Fused silica was used as the solid substrate because of its high transparency, low refractive index, and low chemical activity. The first experiment was to study how SHG from the interface was varied when liquids of different dielectric constants were used. This allowed us to evaluate the importance of the nonlocal contribution to the surface nonlinearity. The second set of experiments was to study SHG from interfaces with monolayers of selective adsorbates. This enabled us to assess the importance of the local contribution to the surface nonlinearity from the molecular monolayers.

The experiments were carried out by focusing the laser beam (at 1.06 or 0.532 μm) on the liquid-solid interface through the fused-silica substrate, and monitoring the SH signal in the reflected direction. A *Q*-switched Nd:YAG laser system (where YAG denotes yttrium aluminum garnet) was used as the pump. The liquids used were all transparent at both ω and 2ω.

To see whether the bulk term in Eq. (3) is significant, we compared the SH signal reflected from the air—fused-quartz interface with the fundamental beam incident from the air side to that with the fundamental beam incident from the fused-quartz side. In the former case, the only bulk contribution was from the air and should be negligibly small. In the latter case, the bulk contribution was from the fused quartz. The nonlinearities in the two geometries were found to be nearly equal, indicating that the bulk contribution from the fused quartz in Eq. (3) was at most 10% of the surface contribution. This shows that by measuring the *s*-polarized SH output, we could study exclusively the surface contribution to the SHG as characterized by $\chi^{(2)}_{s,yzy}$.

A. Study of liquid—fused-quartz interfaces

We measured SHG from the interfaces of fused quartz with a number of liquids. The liquids were chosen to be chemically inactive with quartz and to have their dielectric constants $\epsilon(\omega)$ varied from 1.45 to 2.3, as compared with the dielectric constant of 2.1 for fused quartz. This was to show, at such interfaces, how significant the nonlocal contribution to the surface nonlinearity would be. The liquids chosen are listed in Table I. Before each measurement, the quartz substrate was cleaned in an oxidizing solution ($H_2SO_4 + H_2O_2$), rinsed in distilled water, and dried by N_2 gas. The SH signal from the liquid-solid interface was always calibrated against that from the air-solid interface.

Figures 1(a) and 1(b) and Tables I(a) and I(b) describe the surface susceptibiities deduced from the surface SHG measurements of various interfaces using pump laser wavelengths at 1.06 and 0.53 μm, respectively. Both sets of data show a clear decrease of the interface nonlinearity with a better matching of the dielectric constants of the liquid and solid. Thus we can immediately conclude that, for these interfaces, the surface nonlinearity is dominated

TABLE I: Experimental values corresponding to the points plotted in Figs. 1(a) and (1b).

Liquid	Dielectric constant $\epsilon(\omega)$	$\left\lvert\frac{\chi_{\mathrm{LFS}}{}^{a}}{\chi_{\mathrm{AFS}}{}^{b}}\right\rvert$
	(a)	
N_2 (77 K)	1.452	0.85
Methanol	1.76	0.45
Water	1.78	0.16
Ethanol	1.855	0.41
Trimethylpentane	1.96	0.15
Cyclohexane	1.937	0.12
Glycerol	2.18	0.28
Fused silica	2.13	
	(b)	
N_2 (77 K)	1.42	0.58
Methanol	1.73	0.29
Water	1.75	0.28
Acetone	1.8	0.19
Trimethylpentane	1.92	0.14
Dichloroethane	2.06	0.13
Glycerol	2.13	0.19
Benzene	2.31	0.51
Fused silica	2.11	

[a] LFS denotes liquid—fused-silica interface.
[b] AFS denotes air—fused-silica interface.

by the nonlocal contribution. The data at 0.53 μm are much more scattered. This is presumably because 2ω in this case is near resonance, and the resonant enhancement of the nonlocal contribution is different for different molecules. The data at 1.06 μm are much less influenced by resonance, and they do vary more smoothly with the liquid dielectric constant. We will therefore focus on these data for a more qualitative discussion below.

Figure 1(a) shows that when the liquid dielectric constant $\epsilon(\omega)$ is close to the dielectric constant of the fused quartz, the observed surface nonlinearity reduces to a rather small value. This result indicates that the electric-dipole (local) contribution to $\chi^{(2)}_{s,yzy}$, the χ^{D}_{yzy} term in Eq. (9), cannot be more than 25% of the nonlocal contribution described by the χ^{Q} and χ^{D}_{A} terms in Eq. (9). If we extrapolate the data to the point of $\epsilon(\omega)=\epsilon(\text{quartz})=2.1$, we find $\chi^{(2)}_{x,yzy}$ nonzero. This residual surface nonlinearity comes in general, from the sum of the χ^{D} and χ^{Q} terms in Eq. (9). The χ^{Q} contribution can, in principle, be obtained from Eq. (10) if the bulk quadrupole nonlinear susceptibilities $\chi^{Q}_{zyzy}(0^{-})$ and $\chi^{Q}_{zyzy}(0^{+})$ for the liquid and fused quartz, respectively, are known. The electric-dipole (χ^{D}) contribution can then be deduced from the data. Unfortunately, these χ^{Q} values are not available in the literature. We anticipate that $\chi^{Q}(\text{liquid})\sim\chi^{Q}(\text{quartz})$ for liquids with $\epsilon(\text{liquid})\sim\epsilon(\text{quartz})$. If we simply assume $\chi^{Q}(\text{liquid})=\chi^{Q}(\text{quartz})$, then we find from the data in Fig. 1(a) that the local contribution (from χ^{D}) is about 25% of the nonlocal contribution.

To try to fit the data in Fig. 1(b), we devise a simple model. We assume $s(z)$ varies linearly from $1/\epsilon_1$ to $1/\epsilon_2$ across the interface layer spanned from $z=-d/2$ to $d/2$. We also assume that the electric-dipole term $\chi^{D}_{yzy}\equiv A$ comes from the surface layer of the quartz only. In the low-frequency approximation, it has been shown that the electric-quadrupole nonlinear susceptibility of a medium of dielectric constant ϵ is proportional to $(1-\epsilon)^2$ (Ref. 5). Thus we simply assume

$$\chi^{D}_{Ayzy}=B(1-\epsilon_2)^2\Theta(z>0)+B(1-\epsilon_2)^2\Theta(z<0)$$

and

$$\chi^{Q}_{zyzy}=C(1-\epsilon_2)^2\Theta(z>0)+C(1-\epsilon_1)^2\Theta(z<0)\ ,$$

where Θ is a unit step function. Using Eq. (9), we find a reasonable fit with the data in Fig. 1(b) with $A=-0.2$,

TABLE II. Experimental result for rhodamine 6 G and DMOAP.

Adsorbate	λ_{exc} (μm)	$\frac{\chi_{\mathrm{LFS}}{}^{a}}{\chi_{\mathrm{AFS}}{}^{b}}$	Liquid
Rhodamine	1.06	1.19±0.05	2.2.4-trimethylpentane
DMOAP	0.532	0.17±0.05	Water

[a] LFS denotes liquid—fused-silica interface.
[b] AFS denotes air—fused-silica interface.

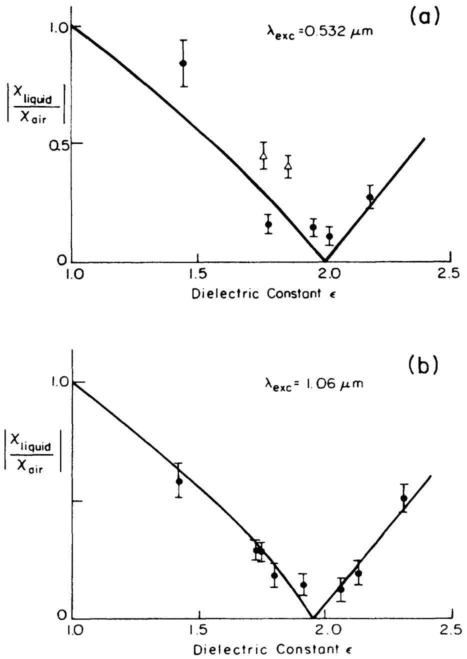

FIG. 1. (a) Ratio of the interface susceptibility of a fused-silica—liquid interface to a fused-silica—air interface ($\lambda_{exc}=0.532$ μm), (b) same plot as (a), but for an excitation wavelength of 1.06 μ.

$B=1.3$, and $C=-1.3$.

The absolute value of the effective surface nonlinearity at the air-quartz interface was measured to be $\chi_{s,yzy}\simeq 2.7\times 10^{-17}$ esu/cm^2. The corresponding electric-dipole part is $\chi^{D}_{yzy}/\epsilon_1 \simeq 5.7\times 10^{-18}$ esu/cm^2. As a comparison, the effective nonlinearity of a layer of crystalline quartz with the thickness of a unit cell (5.4 Å) and the z axis normal to the plane would be $\chi^{D}_{xxx}/\epsilon_1 = 4.5\times 10^{-17}$ esu/cm^2.

Although the model used is crude, it reaffirms our earlier statement that the origin of the surface SHG from an air—fused-quartz interface is mostly a nonlinearity of the electric-quadrupole type. The equality of B and $-C$ is not totally justified either by our experimental accuracy or by our simple model. We, however, notice that if the quadrupole nonlinearity could be considered as arising from an orientational average of the dipole nonlinearity of a group of SiO$_2$ molecules, the coefficients B and $-C$ would indeed be equal.

B. Study of adsorbed molecules on fused quartz

In this section we present results of monolayers of molecular adsorbates on liquid (air)—fused-silica interfaces. We want to see whether the molecular adsorbates contribute to the surface nonlinearity via the field discontinuity at the surface or the local molecular nonlinearity itself. It should be remarked that in the present case the molecular monolayer only affects the first (electric-dipole) and third (electric-quadrupole via field discontinuity) terms in Eq. (9).

We have studied three different adsorbed molecules: rhodamine 6G, n,n-dimethyl-n-octadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP), and p-nitrobenzoic acid (PNBA), all of which can form a stable monolayer on quartz. In all cases we compared the SH signal from molecules adsorbed at a liquid-quartz interface to that at an air-quartz interface. The liquid used would not dissolve the molecules and should leave the molecular monolayer at the interface unmodified. The ratio of the two signals should be close to 1 if the electric-dipole molecular nonlinearity dominates, but should be appreciably less than 1 if the field discontinuity term dominates as the mismatch of the refractive indices is reduced at a liquid-quartz interface. Each system studied was a combination of a stable monolayer on the fused-silica surface (rhodamine 6G, DMOAP, PNBA) and a liquid which would leave either the monolayer or the average coverage unmodified.

The rhodamine 6G monolayer was spin coated from an ethanol solution onto a fused-silica substrate. SHG was measured on such a sample in air and then under a thin layer ($\sim$2 mm) of 2,2,4-trimethylpentane (TMP). By making the measurement in a short time, the monolayer did not appear to be modified (less than 5% change after three experimental cycles). Since 2ω ($\lambda=1.06$ μm) is at resonance with the $S_0 \rightarrow S_1$ transition, the signal was very strong[8,9] and SHG from the substrate could be neglected. We found in this case that the ratio of the surface nonlinearities for the two interfaces was about 1.2 (see Table II). If the electric-quadrupole contribution due to field discontinuity had dominated, we would have observed a ratio of 0.09 according to Eq. (9). Consequently, this result indicates that in the above case the electric-dipole contribution of the rhodamine 6G monolayer to the surface nonlinearity actually dominates.

The DMOAP is a silane surfactant often used as a surface coupling agent for alignment of liquid crystals.[10] The sample of DMOAP on fused quartz was prepared by use of the usual dipping method followed by curing in an

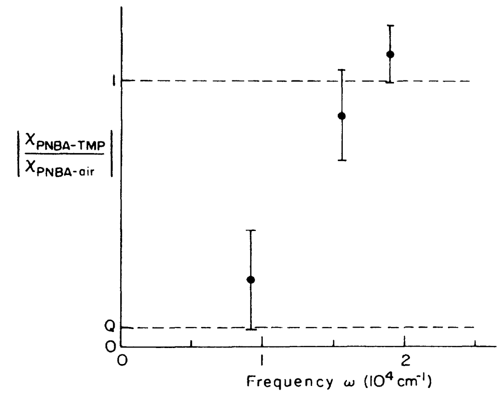

FIG. 2. Plot of the ratio of the PNBA monolayer nonlinear susceptibility of a fused-silica—TMP interface to a fused-silica—air interface at different excitation frequencies.

TABLE III. Experimental values for PNBA. Note: Q is defined from Eq. (9) as $Q=|(1/\epsilon_{\text{quartz}}-1/\epsilon_{\text{liquid}})/(1/\epsilon_{\text{quartz}}-1)|$.

λ_{exc}	Without PNBA		With PNBA		PNBA	
(μm)	$\|\chi_{\text{AFS}}{}^{a}\|$	$\|\chi_{\text{TMPFS}}{}^{b}\|$	$\|\chi_{\text{AFS}}\|$	$\|\chi_{\text{TMPFS}}\|$	phase	$\left\|\frac{\chi_{\text{PNBA-TMPFS}}}{\chi_{\text{PNBA-AFS}}}\right\|$
0.532	1	0.15±0.05	4.3±0.2	4.65±0.2	$\pi/2$	1.1 ±0.1
0.640	1	0.15±0.05	3.2±0.2	2.06±0.2	0	0.87±0.17
1.06	1	0.17±0.03	1.4±0.03	0.27±0.02	0	0.25±0.2

[a] AFS denotes air—fused-silica interface.

[b] TMPFS denotes TMP—fused-silica interface.

oven under nitrogen atmosphere.[10] This method insures that about a monolayer is chemically bonded to the quartz surface. Because this surfactant is strongly hydrophobic, we could study DMOAP adsorbed at a water—fused-quartz interface. In this case the excitation wavelength used was 0.532 μm; both ω and 2ω are nonresonant. The SH signal from a DMOAP-covered fused-silica surface was about two times that from a cleaned fused-silica surface. With the sample immersed in water, the susceptibility decreased from 1 to 0.17, agreeing well with what one would expect from Eq. (9), assuming only electric-quadrupole response. This strong decrease of the signal indicates that the DMOAP monolayer does not give a significant electric-dipole contribution to the surface nonlinearity. This is reasonable since DMOAP consists essentially of a long alkane chain which has a very small intrinsic second-order nonlinearity.

The possibility for two kinds of molecular adsorbates to show either a "dipole" or "quadrupole" nonlinearity led us to the idea that a single molecule could show either behavior depending on the excitation frequency. For this reason, we studied PNBA molecules adsorbed on fused silica. Theoretical calculation on *p*-nitroaniline, which closely resembles PNBA, has shown that its second-order nonlinearity is strongly enhanced when the harmonic frequency is in resonance with the first strongly absorbing ground-state $\rightarrow A_1$ transition.[11] We may expect that PNBA exhibits a "dipole"-type nonlinearity when 2ω is close to resonance with such a transition and a "quadrupole"-type nonlinearity far away from resonance. This is indeed what we observed, as shown in Fig. 2. The absorption maximum of the ground-state $\rightarrow A_1$ transition of PNBA lies around 260 nm. We found that at the excitation wavelengths of both 532 and 640 nm, the ratios of the surface nonlinear susceptibilities at the air/quartz and liquid-TMP—quartz interfaces were close to 1, but dropped to ~ 0.25 with the 1.06 μm excitation.

In this experiment, the liquid used was 2,2,4-trimethylpentane again. However this liquid, used pure, would slowly dissolve a PNBA monolayer (~ 5 min.). Consequently, to prevent any modification of the monolayer coverage, we used a saturated solution of PNBA in this liquid. From our results (Fig. 2, Table III), we conclude that the 2ω resonance with the ground-state $\rightarrow A_1$ transition must be responsible for the electric-dipole nonlinearity of PNBA observed at 532 and 640 nm. This can be understood since the transition is electric-dipole allowed and the ground and excited states involved in the transition have very different dipole moments.

IV. DISCUSSION

From the above experiments we have shown that the surface nonlinear susceptibility of an interface or an adsorbed molecular layer comes from local structural asymmetry as well as nonlocal field discontinuity across the interface. This could be important in the analysis of the SHG results. For example, to use SHG as a tool to determine the orientation of adsorbed molecules, it is more tractable if one can be sure that the electric-dipole nonlinearity along a certain bond or bonds dominates the molecular nonlinearity. It appears that orientational studies of adsorbed molecules can be most easily carried out for large asymmetric molecules using a 2ω resonance with a strong dipole-allowed transition. In that case, not only would the number of relevant components of $\chi^{(2)}$ decrease, but also the overall signal strength and the electric-dipole character of the molecular nonlinearity would both increase. For small adsorbed molecules or symmetric molecules, or molecules with no delocalized electrons, the electric-quadrupole nonlinearity could be dominant if both ω and 2ω are away from resonance with electric-dipole-allowed transitions.

As far as the substrate is concerned, glass seems to have a surface nonlinearity dominated by the nonlocal electric-quadrupole contribution unless its refractive index is matched at the surface. Fused quartz is an example. Liquid also possesses a surface nonlinearity dominated by the nonlocal contribution if it does not have a surface layer of molecules with significant polar ordering. Crystalline solids, however, may have a surface layer structure short of inversion symmetry, and hence a surface nonlinearity dominated by the local electric-dipole contribution. Silicon and germanium are good examples. The dangling bonds, which are highly asymmetric, on the clean surfaces are responsible for the large surface nonlinearities observed on Si and Ge. When they are quenched, the nonlinearity drops appreciably. We note that the field discontinuity at air-Si and air-Ge interfaces is very significant because of the large dielectric constants of Si and Ge. Even so, its contribution to the surface nonlinearity seems to be not so important, at least for the clean surfaces. Metal crystals also possess large surface nonlinearities, which can be crudely decomposed into a part due to free electrons and a part due to bound electrons. The free-electron part contributes to the nonlocal surface nonlinearity, while the bound electrons reflecting the structural asymmetry could contribute to the local surface nonlinearity. Adsorption of molecules on a metal surface may drastically modify the electronic structure of the surface. It will then lead to a significant change of the surface nonlinearity.[12]

V. CONCLUSION

We have demonstrated in this paper, by SHG experiments on a few simple systems, that structural asymmetry and field discontinuity both contribute to the surface nonlinearity. It is seen that at liquid and fused-quartz interfaces with no polar ordering of molecules in the surface layer, the surface nonlinearity is dominated by the electric-quadrupole contribution arising from field discontinuity if the refractive indices are not matched at the interface. For a molecular layer adsorbed at an interface, the electric-dipole contribution due to structural asymmetry dominates if the molecules have a significant polar ordering and either the fundamental or the second-harmonic frequency is close to an electric-dipole-allowed transition. These results can be qualitatively extended to include other solid or fluid substrates. In applying SHG to surface studies, they are important to be taken into consideration for proper interpretation of the experimental observations.

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