Reconsideration of Second Harmonic Generation from neat Air/Water Interface: Broken of Kleinman Symmetry from Dipolar Contribution

Wen-kai Zhang‡, De-sheng Zheng†, Yan-yan Xu†, Hong-tao Bian†, Yuan Guo, and Hong-fei Wang∗

State Key Laboratory of Molecular Reaction Dynamics,
Institute of Chemistry, the Chinese Academy of Sciences, Beijing, China, 100080

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It has been generally accepted that there are significant quadrupolar and bulk contributions to the second harmonic generation (SHG) reflected from the neat air/water interface, as well as common liquid interfaces. Because there has been no general methodology to determine the quadrupolar and bulk contributions to the SHG signal from a liquid interface, this conclusion was reached based on the following two experimental phenomena. Namely, the broken of the macroscopic Kleinman symmetry, and the significant temperature dependence of the SHG signal from the neat air/water interface. However, because sum frequency generation vibrational spectroscopy (SFG-VS) measurement of the neat air/water interface observed no apparent temperature dependence, the temperature dependence in the SHG measurement has been reexamined and proven to be an experimental artifact. Here we present a complete microscopic analysis of the susceptibility tensors of the air/water interface, and show that dipolar contribution alone can be used to address the issue of broken of the macroscopic Kleinman symmetry at the neat air/water interface. Using this analysis, the orientation of the water molecules at the interface can be obtained, and it is consistent with the measurement from SFG-VS. Therefore, the key rationales to conclude significantly quadrupolar and bulk contributions to the SHG signal of the neat air/water interface can no longer be considered as valid as before. This new understanding of the air/water interface can shed light on our understanding of the nonlinear optical responses from other molecular interfaces as well.

I. INTRODUCTION

Since Shen and his co-workers established that the second harmonic generation (SHG) from an interface can be dominated with the electric dipolar contribution of the interfacial molecular layers, SHG has been widely used as the spectroscopic probe for molecular orientation, structure, spectroscopy and dynamics of liquid/vapor interfaces as well as other interfaces, because SHG is electric-dipole forbidden in the centrosymmetric bulk media.1,2,3,5,6,7,8,9,10,11,12,13,14,15 In the early days of the development of SHG for interface studies, it has been fully realized that, in applying SHG to real problems, it is important to know how to assess the relative magnitudes of the interface (local) contribution and the still possibly significant bulk electric-quadrupole and magnetic-dipole (nonlocal) contributions to the SHG signal.1,3,12,13,14,15 Even though there were exchanges of debates on whether SHG can be an effective probe for isotropic liquid interfaces, i.e. whether the bulk contribution is negligible,16,17,18,19,20 it has been generally accepted that it is impossible to separate the bulk contribution from the total SHG signal.15,19,21 Over the past two decades, theoretical treatment has shown that there is no general solution to this problem, and it is often not known a priori in interface SHG and sum frequency generation vibrational spectroscopy (SFG-VS) studies whether in an interface system interfacial contribution is dominant over that of the bulk, or not.12,22 Recently, Morita proposed a formulation towards computation of quadrupolar contribution in SFG-VS, which can also be used for SHG. However, no computational result has been reported so far.

On the other hand, a number of experimental studies have indicated that ‘...in the case of insulators and liquids with ε2 ∼ 3, the bulk contribution may still be appreciable.’13 and ‘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.’23 Thus, it generally nullified the possibility for using non-resonant SHG to obtain detailed molecular information for pure liquid interfaces, and the SHG study on the neat air/water interface is one of the benchmark examples. This is also why the majority of literatures on SHG applications are mainly on near resonant chromophores at various interfaces.

The first neat liquid interface studied with SHG experiment is the neat air/water interface by Goh et al.24 In this and the following works, two basic phenomena of the neat air/water interface were observed. One is the significant temperature dependence of the SHG signal (the SHG intensity dropped more than 50% when temperature was changed from 283K to 353K), and the other is the broken of the Kleinman symmetry, i.e. \( \chi_{zzz} ≈ 2.3 \chi_{zzz} \) at 293K.22 Since it was generally believed that the Kleinman symmetry rule for dipolar susceptibility states that in the static limit, i.e. far from electronic resonance, there is \( \chi_{zzz} = \chi_{zzz} \) the broken of Kleinman sym-

†Also Graduate School of the Chinese Academy of Sciences
*Author to whom correspondence should be addressed. E-mail: hongfei@mrdlab.icas.ac.cn. Tel. 86-10-62555347, Fax 86-10-62563167.
metry for the neat air/water interface was believed to indicate a significant quadrupole (bulk) contribution. In addition to the broken of Kleinman symmetry, the strong temperature dependence was also believed to indicate significant quadrupolar contribution. The temperature dependence was further used to separate the dipolar (interface or local) contributions and the quadrupolar (bulk or nonlocal) contributions, because the dipolar part should strongly depend on the absolute orientation of the water molecules, whereas the quadrupolar contribution should only be weakly dependent on such. Using a simple model, Goh et al. further estimated that the energy that causes a net absolute orientation of water molecules at the interface to be about $\frac{1}{2}kT$ at room temperature.

However, the temperature dependence result in SHG measurement was questioned by Du et al. with the first SFG-VS investigation of the neat air/water interface, where the vibrational spectra of the interfacial free OH group was directly measured. Temperature dependence of the SFG spectrum of the air/water interface showed no significant change over the same temperature range from 283K to 353K. As reported, Du et al. also repeated the SHG temperature dependent experiment of the neat air/water interface from 283K to 318K, and they observed no change of $\chi_{zzz}$ within the experimental uncertainty of ±10%, while a 50% decrease was expected from the Goh et al.3,4,26 results.

On the request by Professor Y. R. Shen, Professor K. B. Eisenthal's group repeated the SHG temperature experiment of the neat air/water interface in January of 1993, and found that in the same temperature range, $\chi_{zzz}$ decreases only by less than 10% and $\chi_{zzz}$ decreases by about 10%, as reported in Du et al. One of us (Hong-fei Wang) was then the student in the Eisenthal group who was responsible for repeating the SHG temperature dependence measurement. It was found that the strong SHG temperature dependence reported previously was an experimental artifact due to the uncontrolled condensation of water vapor on the internal surfaces of the two quartz windows of the enclosed temperature controlled cell made of brass. The condensation became visible when the internal temperature of the cell is higher than the room temperature controlled at 22.0±1.0°C, and more condensation was formed when the temperature difference became larger before it reached a steady state. Thus, the SHG signal drop became more pronounced with the increase of the degree of condensation until it levelled off around 310K. Heating of the external surface of the temperature cell with slightly higher external temperature than the internal temperature can prevent condensation on the internal surface of the quartz windows. After getting rid of the condensation, no SHG signal remained at room temperature.

Recently, with the knowledge that Goh et al.'s SHG temperature dependence results were not repeatable, Fordyce et al. reported a new measurement that there was a 20% of the SHG signal temperature drop of the neat air/water interface from 293K to 343K. Careful examination of this report makes us believe that without effective condensation control for the temperature cell windows, this work might have also been subjected to the same experimental artifact as that of Goh et al. Nevertheless, all the SHG experimental results confirmed the validity of the broken of Kleinman symmetry for the neat air/water interface.

Because the magnitude of the temperature dependence of the SHG signal was believed to indicate the magnitude of the dipolar (local) contribution to the SHG signal, no apparent temperature dependence could lead to the conclusion that the apparent dipolar contribution to the SHG signal from the neat air/water interface is negligible. In addition, the broken of the Kleinman symmetry was also an indication of significant quadrupolar (nonlocal) contribution to the SHG signal from the neat air/water interface. Therefore, it seems reasonable to conclude that all the SHG signal from the neat air/water interface was quadrupolar contribution in nature! Indeed, Bloembergen et al. did conclude as early as 1968 that the 'SHG reflection from media with inversion symmetry is described rather well by the quadrupole-type nonlinear properties calculated for the homogeneous bulk material with a abrupt discontinuity at the boundary.' However, Bloembergen et al.'s discussion was on experimental results and theoretical analysis of metal and alkali halides surfaces, which possess relatively high density of valence electrons, but not on surfaces of normal liquid. Such a strong statement on metal and alkali halides surfaces by Bloembergen et al. was firstly questioned by Brown et al.'s SHG experiment on adsorbed surface layer on silver in 1969, but only fundamentally modified more than a decade later, after Y. R. Shen's group demonstrated systematically in the early 1980's that surface SHG can be treated as radiation from a nonlinear polarization sheet induced by an incoming wave at the surface, besides comparable quadrupole (bulk) contributions. This development undoubtedly assured the surface monolayer sensitivity of surface SHG for all kinds of surfaces. These works by Y. R. Shen and his colleagues heralded the beginning of systematic interface studies with nonlinear optical techniques including studies of the longtime nail-biting liquid interfaces. These twists in the historical development of surface SHG demonstrated the complexity and difficulty on the evaluation of relative bulk and surface contributions to surface SHG signal.

Now, if the above conjecture on the pure quadrupolar (bulk) contribution to SHG from neat air/water interface could be held true, the observed SHG signal could have no surface specificity and should not have been used to study the molecular orientation and structure of the
air/water interface. And this can also be the same for other liquid interfaces. The consequence is that the whole effort of using SHG for non-resonant liquid interface studies should have been nullified. Indeed, in the past decade, using SHG to study neat air/liquid and liquid/liquid interfaces has been rare.3,11,12 This situation would persist unless the widely held assumption3,4,9,12 that the broken of the Kleinman symmetry is an indication of significant quadrupolar (nonlocal) contribution to the SHG signal from an interface, is generally not true. Examination of the history of the Kleinman symmetry of the nonlinear microscopic polarizability and macroscopic susceptibility tensors indeed raised more questions on the general validity of this symmetry relationship which first discussed by Kleinman in 1962.25,34

The validity of the Kleinman symmetry of the second order nonlinear susceptibility tensors was thoroughly discussed by Franken and Ward as early as in 1963.25 and most recently by Dailey et al.26 As pointed out by Franken and Ward, Kleinman suggested that for a material transparent (far from resonance) to the fundamental and the SH frequencies, an additional symmetry condition of $\chi_{ijk} = \chi_{jik}$ exists, where the first index is for the SH frequency, and the second and third indexes are for the fundamental frequency.35 To translate this for water, $\chi_{xzx} = \chi_{xxz}$ should hold be true if the Kleinman symmetry is valid when both fundamental and the SH frequencies are far from resonance with the water molecule transition frequencies. It was well recognized by Franken and Ward that the presence of dispersion can destroy the validity of the Kleinman symmetry, and using a quantum mechanical formulation of the dipolar susceptibility tensors they further pointed out that even a few percent dispersion can seriously damage the validity of Kleinman symmetry. It was further demonstrated by Franken and Ward that for the case of quartz with the fundamental frequency at 694.3 nm of the Ruby laser, even though the dispersion is only about 2%, the broken of the Kleinman symmetry can be as significant as 30% by considering the dipolar contribution only.25 This undoubtedly suggested a general breakdown of the Kleinman symmetry for general materials and molecules. This is also why Franken and Ward25 as well as Ron Shen27 called it as Kleinman’s conjecture instead of Kleinman Symmetry34. Therefore, in the study of real molecular systems, Kleinman symmetry should generally fail under the dipole approximation.36,38 Recently, using the Kramers-Kronig dispersion relations, Dailey et al. again discussed this general failure of Kleinman symmetry relationship in nonlinear susceptibility tensors of molecular systems, and they further listed numerous experimental disagreements with the Kleinman symmetry relationship under non-resonant conditions in the literatures.39 Thus, it is clear that the broken of Kleinman symmetry can never be used as the criterion for the existence of quadrupolar (bulk) contribution to SHG signal. However, the validity of the Kleinman symmetry had been overvalued3,4,9,12 due to the lack of awareness about the original work by Franken and Ward.25

In Franken and Ward’s discussion of quartz crystal, the macroscopic symmetry of the crystal is the same as the microscopic symmetry of the unit cell. However, for molecular system, the macroscopic symmetry of the molecular system and the microscopic symmetry of the molecule are usually not identical, especially for the liquid interfaces which usually have rotationally isotropic symmetry around the interface normal, no matter what symmetry each individual molecule may possess. Therefore, the connection between the microscopic and macroscopic Kleinman symmetry relationship is not as straightforward as that for crystals. Recently, Simpson et al. have tried to bridge this gap by working on the molecular and surface hyperpolarizability of oriented chromophores of different symmetries and different electronic transitions.36-39,40 These works can certainly provide good references for dealing with complicated relationships of susceptibility tensors in SHG and SFG studies of molecular interfaces.

For the neat air/water interface, Goh et al. pointed out that derivation of the expressions of biaxial molecule ($C_{2v}$ symmetry) might help interpretation of the SHG signal from the air/water interface.41 This was indeed pursued briefly for the air/water interface42 but it was ultimately carried away by the observed temperature dependence phenomenon, which seemingly indicated significant quadrupolar contributions to the SHG signal.34 Besides, the major obstacle in the advance of SHG technique for surface studies has always been the lack of microscopic understanding of the surface nonlinear susceptibility $\chi_{ijk}$.42

In this report, after brief discussion of the basic theory of SHG, we shall first present the discussion on the connection between the microscopic polarizability tensors of the water molecule and the macroscopic susceptibility tensors. Then we shall discuss the general considerations regarding the interface and bulk contributions to the SHG from an interface. Finally we shall present the treatment on the SHG measurement with the proper formulation of the microscopic polarizability tensors of the water molecule, which gives well description with the dipolar nature of the SHG response from the neat air/water interface. The major conclusion is that with explicit treatment of the molecular symmetry, dipolar (interface) contribution alone can provide satisfactory explanation to the observed SHG signal from the neat air/water interface. We shall show that not only detailed information on molecular orientation can be obtained from polarization SHG measurement of the neat air/water interface, but also such treatment can be generally applied to other molecular interfaces as well. This new understanding of the air/water interface can shed light on our understandings of the nonlinear optical responses from other molecular interfaces.
II. THEORETICAL BACKGROUND

A. Basic Theory

The basic theory of SHG as a general surface analytical probe has been well described in the literatures. However, detailed treatment of the experimental data in different polarizations has not been usual. Generally, the SHG Intensity $I(2\omega)$ reflected from an interface is given below:

$$I(2\omega) = \frac{32\pi^3 \omega^2 \sec^2 \Omega}{c_0 n_1(\omega)n_1(2\omega)} |\chi_{\text{eff}}|^2 I_\omega^2$$

$$\chi_{\text{eff}} = [L(2\omega) : \dot{e}(2\omega)] \chi: [L(\omega) : \dot{e}(\omega)], [L(\omega) : \dot{e}(\omega)]$$

In Equation $I_\omega$ is the incoming laser intensity, $c_0$ is the speed of the light in the vacuum, and $\Omega$ is the incident angle from the surface normal. In Equation $\chi$ is the macroscopic second-order susceptibility tensor, which has $3 \times 3 \times 3 = 27$ elements; $\dot{e}(2\omega)$ and $\dot{e}(\omega)$ are the unit vector of the electric field at $2\omega$ and $\omega$; $L(2\omega)$ and $L(\omega)$ are the tensorial Fresnel factors for $2\omega$ and $\omega$, respectively.

It is important to realize that $\chi_{\text{eff}}$ contains all molecular information of SHG measurement. Actually $\chi_{\text{eff}}$ is the point product of the observation vector $[L(2\omega) : \dot{e}(2\omega)]$ and the second order polarization vector $P^{(2)} = \chi: [L(\omega) : \dot{e}(\omega)], [L(\omega) : \dot{e}(\omega)]$. In the SHG experiment, the field vectors of the incoming and out-going light beams are controlled by the experimenter; once these field vectors are fixed, the tensorial Fresnel factors are also fixed quantities. So the SHG experiment measures the SHG intensity and provides the information of the macroscopic susceptibility of the molecular system.

In SHG experiment, there are three independent polarization measurement, namely, s-in/p-out (Isp), 45°-in/s-out (I45°s) and the p-in/p-out (Ipp). Here, in the experimental coordinate system ($x$, $y$, $z$), $z$ is the interface normal, and we choose $xz$ plane as the incident plane. Subsequently, polarization is defined as polarization within the $xz$ plane, and $s$ is perpendicular to the $xz$ plane. If the microscopic local field factors of the molecular layer are considered, the $\chi_{\text{eff}}$ of these three polarizations should take the following forms:

$$\chi_{\text{eff,sp}} = L_{zz}(2\omega)L_{yy}^2(\omega)l_{zz}(2\omega)l_{yy}^2(\omega) \sin \Omega \chi_{zyy}$$

$$\chi_{\text{eff,45°s}} = L_{yy}(2\omega)L_{zz}(2\omega)L_{yy}(\omega) \times l_{yy}(2\omega)l_{zz}(\omega)l_{yy}(\omega) \sin \Omega \chi_{yzy}$$

$$\chi_{\text{eff,pp}} = L_{zz}(2\omega)L_{xx}^2(\omega)l_{zz}(2\omega)l_{xx}^2(\omega) \sin \Omega \cos^2 \Omega \chi_{zzz} - 2L_{xx}(2\omega)L_{zz}(\omega)l_{xx}(\omega) \times l_{xx}(2\omega)l_{zz}(\omega)l_{xx}(\omega) \sin \Omega \cos^2 \Omega \chi_{zzz}$$

$$+ L_{zz}(2\omega)L_{zz}^2(\omega)l_{zz}(2\omega)l_{zz}^2(\omega) \sin^3 \Omega \chi_{zzz}$$

where $l_{xx}(\omega)$, $l_{yy}(\omega)$ and $l_{zz}(\omega)$ are the microscopic local field factors at frequency $\omega$.

B. Microscopic and Macroscopic Kleinman Symmetry

Here we discuss the direct connection between the Kleinman symmetry of the microscopic (molecular) polarizability tensor elements $\beta_{lmn}$ and the macroscopic susceptibility tensor elements $\chi_{ijk}$ of the molecular system. Here we only consider the contribution from the dipolar terms.

Under the dipolar approximation, it is known that $\chi_{ijk}$ is generally related to $\beta_{lmn}$ through Euler transformation operation, which is the product of three rotational operations of the molecular coordinates system:

$$\chi_{ijk} = N \sum_{lmn=abc} \langle R_{il}R_{jm}R_{kn} \rangle \beta_{lmn}$$

where $N$ is the interface molecule density, the operator $\langle \rangle$ denotes the rotational ensemble average over the Euler rotation matrix transformation element $R_{\lambda\lambda'}$ from the
molecular coordinate \(X'(a, b, c)\) to the laboratory coordinate \(X(x, y, z)\). The subscript \((i, j, k)\) of the \(\chi_{ijk}\) corresponds to the laboratory coordinate \((x, y, z)\), and the subscript \((l, m, n)\) of the \(\beta_{lmn}\) corresponds to the molecular coordinate \((a, b, c)\). This expression can also be written into the summation over \(\beta_{lmn}\) of each molecule in the molecular system which contributes to \(\chi_{ijk}\).

\[
\chi_{ijk} = \sum_{l=1}^{N} \sum_{lmn=abc} R_{il}^l R_{jm}^l R_{kn}^l \beta_{lmn} \tag{6}
\]

In the most general case there are 27 second order susceptibility tensor elements for \(\chi_{ijk}\) as well as \(\beta_{lmn}\). Because in SHG the two fundamental frequencies are equivalent, the relationship \(\chi_{ijk} = \chi_{ikj}\) and \(\beta_{lmn} = \beta_{mnl}\) are always valid. So in the most general case there are only 18 independent elements for \(\chi_{ijk}\) and \(\beta_{lmn}\), respectively. Kleinman symmetry states that \(\chi_{ijk} = \chi_{ikj}\) for the macroscopic susceptibility tensor elements, and \(\beta_{lmn} = \beta_{mnl}\) for the microscopic polarizability tensor elements. Kleinman symmetry can further reduce the independent elements to the number of 10. Of course, the number of non-zero tensor elements is much smaller than this number.

Because the microscopic Kleinman symmetry relationship requires \(\beta_{lmn} = \beta_{mnl}\), and because the product of the matrix elements always satisfy \(R_{il}^l R_{jm}^l R_{kn}^l = R_{jm}^l R_{il}^l R_{kn}^l\), we immediately have

\[
\chi_{ijk} = \sum_{l=1}^{N} \sum_{lmn=abc} R_{il}^l R_{jm}^l R_{kn}^l \beta_{lmn} = \sum_{l=1}^{N} \sum_{lmn=abc} R_{jm}^l R_{il}^l R_{kn}^l \beta_{mnl} = \chi_{ikj} \tag{7}
\]

This simple transformation proves that the Kleinman symmetry is invariant under arbitrary rotational transformation. Because the rotational transformation is linearly reversible, if the macroscopic Kleinman symmetry holds, the microscopic Kleinman symmetry should also hold, as long as all the molecules in the system can be treated identical. This relationship conceptually simplifies many things when we are trying to compare experimental results with molecular properties in SHG, as well as SFG studies.

Microscopic Kleinman symmetry is valid for uniaxial rod-like molecule, because such molecule has only one non-zero molecular polarizability tensor element \(\beta_{ccc}\). Therefore, any macroscopic system consists of uniaxial molecule shall observe Kleinman symmetry. It was just because the ‘ubiquitous’ usage of uniaxial molecule model in description of nonlinear chromophores, Kleinman symmetry has been generally held true in the past forty years, pointed out precisely by Dailey \textit{et al.}\cite{11} despite the seminal discussion of Franken and Ward in 1963 on the general failure of Kleinman symmetry even for quartz crystal.\cite{12}

\section{SHG from Liquid Interface of Water: the Molecule with \(C_2v\) Symmetry}

Here we present the detailed treatment of the SHG from neat air/water interface considering only the dipolar contribution.

The water molecular belongs to \(C_2v\) symmetry. Therefore, there are seven non-zero microscopic polarizability tensor elements in SHG, namely \(
\beta_{ace}, \beta_{aca}, \beta_{ace} = \beta_{aan}, \beta_{acb}, \beta_{bcb} = \beta_{b, ab, \infty}\). Here the molecular coordinates are defined to have \(c\) axis along the \(C_2\) axis, and to have \(ac\) plane as the molecular plane. For the rotationally isotropic neat air/water interface, there are 7 non-zero elements, i.e., \(\chi_{zzz}, \chi_{xyy}, \chi_{xyz}, \chi_{xzz} = \chi_{zzz}\). Because the twisted angle \(\psi\) and the azimuthal angle \(\phi\) can be considered isotropic, using Eq.\textit{5} and average over Euler angle \(\psi\) and \(\phi\), we have

\[
\begin{align*}
\chi_{zzz} &= \frac{N_s}{2} [((\beta_{aca} + \beta_{cb} - 2\beta_{aca} + 2\beta_{acb} + 2\beta_{bab}) \cos \theta)] \\
&+ (2\beta_{acc} - \beta_{aca} - \beta_{acb} - 2\beta_{aca} + 2\beta_{acb}) \cos^3 \theta \tag{8}
\end{align*}
\]

Because \(\beta_{aca}\) and \(\beta_{acb}\) always go together in these expressions, if \(\beta_{aca} \neq 0\), we define \(r = \frac{\beta_{aca} + \beta_{acb}}{2\beta_{acc}}\); and similarly we define \(s = \frac{\beta_{aca} + \beta_{acb}}{2\beta_{bcc}}\). Then we have

\[
\begin{align*}
\chi_{zzz} &= \frac{N_s}{2} [((\beta_{aca} + \beta_{cb} - 2\beta_{aca} + 2\beta_{acb} + 2\beta_{bab}) \cos \theta)] \\
&+ (2\beta_{acc} - \beta_{aca} - \beta_{acb} - 2\beta_{aca} + 2\beta_{acb}) \cos^3 \theta \tag{9}
\end{align*}
\]

And the \(\chi_{xxx}/\chi_{xxx}\) and \(\chi_{zzz}/\chi_{xxx}\) ratios are

\[
\begin{align*}
\frac{\chi_{xxx}}{\chi_{xxx}} &= \frac{(1 + r - 2s)D - (1 - r - 2s)}{(1 - r)D - (1 - r - 2s)} \tag{10}
\end{align*}
\]

\[
\begin{align*}
\frac{\chi_{zzz}}{\chi_{xxx}} &= \frac{2(r + 2s)D + 2(1 + r - 2s)}{(1 - r)D - (1 - r - 2s)} \tag{11}
\end{align*}
\]

in which \(D = \langle \cos \theta \rangle / \langle \cos^3 \theta \rangle\) is the orientational parameter of the water molecule at the neat air/water interface.\cite{13} It is clear from Eq.\textit{10} that if \(r = s\), then...
\[ \chi_{zzz} = \chi_{xxx} \text{ and vice versa.} \] From the definition, \( r = s \) is equivalent to \( \beta_{aca} + \beta_{cbb} = \beta_{aca} + \beta_{cbb} \), which is the necessary condition for Kleinman symmetry.

When \( r \neq s \), it is clear from Eq.10 that the ratio \( \chi_{xxx}/\chi_{zzz} \neq 1 \) unless \( D = 0 \). However, \( D = 0 \) is physically impossible, therefore, a trivial solution. Thus, \( \chi_{xxx}/\chi_{zzz} \) value not only depends on \( r \) and \( s \), but also on the value of the orientational parameter \( D \). Only when \( D = 1 \), we have \( \chi_{xxx}/\chi_{zzz} = r/s \), which means that the macroscopic and microscopic tensor ratios are equal. Because the two ratios of \( \chi_{xxx}/\chi_{zzz} \) and \( \chi_{zzz}/\chi_{xxx} \) can be obtained from experiment by using Eq.3, and if we know the value for \( r/s \), \( D \) value can be determined by solving the Eq.10 and Eq.11.

Here with the special case that when \( \beta_{ccc} = 0 \), only the ratio \( R = r/s = \beta_{aca}/\beta_{cbb} \) is physically meaningful, and Eq.10 and Eq.11 become into the followings.

\[
\frac{\chi_{xxx}}{\chi_{zzz}} = \frac{(R - 2)D + (R + 2)}{-R*D + (R + 2)} \quad (12)
\]

\[
\frac{\chi_{zzz}}{\chi_{xxx}} = \frac{2(R + 2)D - 2(R + 2)}{-R*D + (R + 2)} \quad (13)
\]

It has been known from quantum mechanical treatment, \( C_{2v} \), molecule must have a low-lying excited electronic state with a transition dipole moment perpendicular or close to perpendicular to the molecular dipole, i.e. along \( a \) or \( b \) axis. This low-lying state belongs to the \( B \)-type irreducible representation, and the dominant molecular polarizability tensors for the \( B \)-type transition can only be either \( \beta_{aca} = \beta_{aca} \) (\( B_1 \)) or \( \beta_{cbb} = \beta_{cbb} \) (\( B_2 \)) in resonance. For water molecule, the first two electronic excited states belongs to \( B_1 \) and \( B_2 \) symmetry, and the transitions are around 140nm-190nm (diffusive) and 124nm (strong), respectively. According to Dai and Thomas, the Kramers-Kronig dispersion relations dictate that even far from resonance, the largest tensor elements for water molecule have to be \( \beta_{aca} = \beta_{aca} \) or \( \beta_{cbb} = \beta_{cbb} \), and the Kleinman symmetry has to be broken. Importantly, because the first two transitions are along \( a \) or \( b \) directions, \( \beta_{xxx} \) is expected to be very small or negligible, comparing to \( \beta_{aca} = \beta_{aca} \), \( \beta_{cbb} = \beta_{cbb} \), \( \beta_{cbb} \) and \( \beta_{xxx} \) terms, according to the quantum mechanical sum-over-states (SOS) treatment of the molecular hyperpolarizabilities. Therefore, the broken of macroscopic Kleinman symmetry for the neat air/water interface reported previously is unavoidable, and can be fully formulated using only dipolar contribution as described in this section.

If \( \beta_{aca} \) term can be very small or negligible as discussed above, Eq.12 and Eq.13 can be used to extract unique \( R \) and \( D \) values.

D. Beyond the Dipolar Contribution

Here we discuss the implication of the above treatment on the dipolar contribution to the total SHG signal.

Detailed treatment on contributions to the total SHG signal from the dipole, quadrupole and field gradient across the interface layer has been well established in the literatures. The dipolar contribution is usually referred as the interface or local contribution, and the other two contributions are generally referred as the bulk or nonlocal contributions. When the upper phase is air, we have,

\[
\chi_{total}^{zzz} = \chi_{s,zzz} - \left( \gamma + \chi_{Q,zzz} \right) \frac{\epsilon'(2\omega)}{\epsilon(2\omega)} \quad (14a)
\]

\[
\chi_{total}^{xxx} = \chi_{s,xxx} - \left( \gamma + \chi_{Q,xxx} \right) \frac{\epsilon'(2\omega)}{\epsilon(2\omega)} \quad (14b)
\]

\[
\chi_{total}^{xxx} = \chi_{s,xxx} - \chi_{Q,xxx} \frac{\epsilon'(\omega)}{\epsilon(\omega)} \quad (14c)
\]

where \( \chi_{total}^{ijk} \) is the total susceptibility tensor element, which includes both the interface and bulk contributions. \( \chi_{s,ijk} \) is the dipolar susceptibility tensor, denoted as \( \chi_{s,ijk} \) in previous sections. \( \gamma \) represents the contribution from the field gradient across the interface. \( \epsilon'(\omega) \), \( \epsilon'(2\omega) \) are the effective optical dielectric constants of the interface layer, and \( \epsilon(\omega) \), \( \epsilon(2\omega) \) are the optical dielectric constants of the bulk liquid. \( \chi_{Q,ijk} \) is the quadrupolar susceptibility tensor components of the bulk medium.

As we have known, the ratios between the three \( \chi_{total}^{ijk} \) in Eq.11 can be determined directly from the SHG measurements. However, in principle the relative contributions to \( \chi_{total}^{ijk} \) from the local and nonlocal terms can not be explicitly estimated. From Eq.11, Here we argue that if the ratios of the \( \chi_{total}^{ijk} \) terms can be quantitatively explained with the dipolar terms, i.e. \( \chi_{s,ijk} \) terms, the contributions from the bulk terms can be very small or negligible. At least, based on the discussions we have so far, all the previous arguments for them to be comparable to the dipolar terms can not be substantiated.

III. EXPERIMENTAL

A broadband tunable mode-locked femtosecond Ti:Sapphire laser system (Tsunami, Spectra-Physics) is used for reflected-geometry SHG measurement. Its high-repetition rate (82MHz) and short pulse-width (80fs) make it suitable for detection of weak second harmonic signals. Its long term power and pulse-width stability also make it easy for quantitative analysis of the SHG data. The optical set-up is typical for SHG experiment. The 800nm fundamental laser beam is focused on the air/water interface at the incident angle of \( \Omega = 70^\circ \), and the SHG signal at 400nm is detected with a high gain photo-multiplier tube (R585, Hamamatsu) and a photon counter (SR400, Stanford). Typically the dark noise level is less than 3 counts/second. The laser power is typically 500mW. The efficiency of the detection system for \( p \) polarization is 1.31 times of that for \( s \) polarization.
A teflon beaker (diameter around 10cm) is used to contain the pure water liquid (Millipore 18.2MΩ·cm). Optical polarization controlling, SHG data acquisition are programmed and controlled with a PC. It takes about 300 seconds to collect the polarization curve. The room temperature is controlled at 22.0 ± 1.0°C, and the humidity of the room is controlled around 40%.

IV. RESULTS AND DISCUSSIONS

A. Calculation of SHG Intensities

Here we present the analysis of the polarization SHG data with the dipolar formulations in Section II. The SHG signal in both \(p\) and \(s\) polarizations are measured with automatic scanning of the input polarization in the full 360°, as presented in Fig. 1. Because the SHG signal from a neat air/liquid interface is usually very small, full range scanning of the input polarization can help improving the accuracy of the SHG intensities measurement in the desired \(sp\), 45°\(s\) and \(pp\) polarizations. The SHG signal is especially small for \(sp\) polarization of air/water interface. With the symmetrical polarization curves as shown in Fig. 1 such small signal can be determined with much better accuracy than previously reported results, where input polarization were only varied between 0° to 90°. The polarization data with full 360° scan range also provides another advantage. It is that the offset of the polarization angle in the SHG experiment, which can cause significant error on the very small SHG signal in \(sp\) polarization, can be accurately determined.

![Fig. 1: 360° polarization SHG measurement of the neat air/water interface at two fixed detection polarizations (open circle for \(p\) detection; closed circle for \(s\) detection). Each point was averaged for three times. The lines are fitting curves.](image)

The data in Fig. 1 should follow the following functions:

\[
I_p = [A \cos^2 \theta + B \sin^2 \theta]^2 \\
I_s = [C \sin(2\theta)]^2
\]

\[\text{(15)}\]

Fitting results for the \(p\) detection curve gave \(A = 14.42 \pm 0.07, B = 2.42 \pm 0.18\), the offset of \(\theta\) is \(\theta_0 = 6.6^\circ \pm 0.4^\circ\); and the \(s\) detection curve gave \(C = 7.17 \pm 0.08\) and \(\theta_0 = 7.2^\circ \pm 0.5^\circ\). Such fitting results gave the following values, \(I_{pp} = 208 \pm 2\), \(I_{sp} = 5.9 \pm 0.9\) and \(I_{45^\circ s} = 51.4 \pm 1.1\). With the \(s\) and \(p\) detection ratio of 1.31, and after corrections with the Fresnel factors and the local field factors (which is essentially no influence), we obtain \(\chi_{zxx}/\chi_{xzz} = 0.30 \pm 0.03\) and \(\chi_{zzz}/\chi_{xzz} = 2.56 \pm 0.06\). These ratios are consistent with the results reported in the literatures (Table II), and the values obtained here should be with better accuracy, as we compared the quality of SHG data with those in the literatures, especially for the very small value of \(I_{sp}\). Nevertheless, because \(I_{sp}\) is very small, its value might have been overestimated in the past literatures. Goh et al. studied these relative phases, and our results are consistent with their report on this issue.

B. Water Molecular Hyperpolarization Tensors

Here we try to estimate the water molecular orientation at the neat air/water interface from the SHG data. In Eq. 10 and Eq. 11 there are three unknown parameters, i.e. \(r\), \(s\) and \(D\). In order to get the value of \(D\), value of either \(r\), \(s\) or \(r/s\) needs to be known \textit{a priori}. Otherwise, \(D\) value can only be estimated for possible \(r/s\) values.

As discussed in Section II.C, \(\beta_{zzz}\) term can be very small or negligible among the 7 nonzero terms of the \(C_{2e}\) water molecule. Now we plug in \(\chi_{zxx}/\chi_{xzz} = 0.30 \pm 0.03\) and \(\chi_{zzz}/\chi_{xzz} = 2.56 \pm 0.06\) in Table II into Eq. 12 and Eq. 13 and we obtain \(R = 0.69 \pm 0.02\) and \(D = 1.72 \pm 0.03\).

TABLE I: The \(\chi_{zxx}/\chi_{xzz}\) and \(\chi_{zzz}/\chi_{xzz}\) ratios from different research groups. The calculated \(R\), \(D\) and \(\theta\) values according to Eq. 12 and Eq. 13 are also listed.

|          | Eisenh*al | Frey†*2 | Girau†*9 | This work |
|----------|-----------|---------|----------|-----------|
| \(\chi_{zxx}/\chi_{xzz}\) | 0.46      | 0.48±0.02(|?) | 0.41     | 0.30±0.03 |
| \(\chi_{zzz}/\chi_{xzz}\) | 1.20      | 3.6±0.5  | 2.56     | 2.56±0.06 |
| \(R\)    | 0.66      | 0.81±0.03| 0.74     | 0.69±0.02 |
| \(D\)    | 1.39      | 1.84±0.07| 1.69     | 1.72±0.02 |
| \(\theta\) | 32.6°     | 42.5°±1.2°| 39.8°    | 40.3°±0.4°|
reported with the known low-lying electronic transition frequency smaller than the resonant frequency can be estimated in Table I. The \( R \) values obtained from previously reported data are all quantitatively consistent with our results.

The result \( R < 1 \) confirms our expectation that \( \beta_{acc} = \beta_{aca} \) or \( \beta_{abc} = \beta_{cab} \) are dominant terms, and the Kleinman symmetry is broken. The fact, that \( \chi_{xxx}/\chi_{zzz} \) is significantly smaller than \( R \), indicated that the degree of broken of the Kleinman symmetry is usually not the same for the microscopic polarizability tensors and the macroscopic susceptibility tensors. From Franken and Ward, \( R \) value for a certain fundamental frequency (\( \omega \)) smaller than the resonant frequency can be estimated with the known low-lying electronic transition frequency (\( \omega_{eg} \)). Franken and Ward defined \( R \) as:

\[
\frac{\chi_{(2)}^{zzz} - \chi_{(2)}^{xxx}}{\chi_{(2)}^{xxx}} \approx \varepsilon \chi_{xyz}
\]

\[\varepsilon \approx \frac{2\omega^2 + \omega_{eg}^2}{\omega_{eg}^2 - 4\omega^2} - 1 \quad (16)
\]

Clearly, \( R = 1/(1 + \varepsilon) \). In our calculation, with laser wavelength as 800nm, and water transition wavelength as 124nm, we obtained \( R = 0.86 \); with laser wavelength as 800nm, and water transition wavelength as 190nm, \( R = 0.70 \). These \( R \) values well agree with our experimental value.

Theoretical calculations have generated scattered values for ratios of hyperpolarizability tensors for the water molecule, when the possibility for broken of Kleinman symmetry was considered. In many of other calculations, Kleinman symmetry was used as a constraining condition. \( \beta_{acc} \) value in all these calculations are usually comparable or even larger than other tensor elements. However, results vary significantly with calculation models used. So far, experimental values was scare for comparison with these calculations. No experimental value for ratio of hyperpolarizability tensors has been available. The experimental value of \( R \) we obtained here can be used for such comparison with calculated results.

In our calculation, if \( \beta_{acc} \) can not be neglected, \( r, s \) and \( D \) can not be uniquely solved with Eq.\( \ref{eq:16} \) \( \text{and} \) Eq.\( \ref{eq:11} \). If we let \( r = 0.5 \), which means \( 2\beta_{ccc} = \beta_{aca} + \beta_{cab} \), then we get \( s = 0.95 \pm 0.04 \), i.e. \( R = 0.53 \pm 0.02 \), and \( D = 1.81 \pm 0.02 \), i.e. \( \theta = 42.0^\circ \pm 0.3^\circ \), from \( \chi_{zzz}/\chi_{xxx} = 0.30 \pm 0.03 \) and \( \chi_{zzz}/\chi_{zzz} = 2.56 \pm 0.06 \). If we allow \( \beta_{acc} \) to be even larger, for example, we let \( r = 0.25 \), then we get \( s = 0.58 \pm 0.03 \), i.e. \( R = 0.43 \pm 0.02 \), and \( D = 2.08 \pm 0.03 \), i.e. \( \theta = 46.1^\circ \pm 0.4^\circ \). These values indicated that even though \( r, s \) and \( D \) values can not be uniquely determined with experimental values of \( \chi_{zzz}/\chi_{xxx} \) and \( \chi_{zzz}/\chi_{zzz} \), the \( R \) and \( D \) values are not very sensitive to the nonzero \( \beta_{ccc} \) values used. Especially, the calculated \( \theta \) value changed only less than 6 degrees.

Here we discussed how to extract polarizability tensor ratio \( R \) or \( r \) and \( s \), from the SHG experimental data considering of dipolar (local or interface) contribution only. The values we obtained are self-consistent, and can provide a good microscopic description of the SHG polarization signal from the neat air/water interface. These analyses indicate that quadrupole (nonlocal or bulk) contributions to SHG signal from air/water interface can be very small or negligible, even though we cannot say that such contributions has to be negligible. Most importantly, these analyses demonstrate that the previous rationales and evidences\( \ref{eq:16},\ref{eq:11} \) can no longer be used to draw conclusion for significant contributions of the bulk terms to the SHG signal from the neat air/water interface.

### C. Water Molecule Orientation at Neat Air/Water Interface

Here we discuss the orientation of water molecule at the neat air/water interface in the light of the SHG analysis above.

As we have known, there are at least two kinds of water molecules at the neat air/water interface from the SFG-VS experimental studies. Namely, one kind (straddle-type) is with one free O-H bond sticking out of the liquid interface and with its dipole vector (from positive to negative) point almost parallel to the air/water interface; and the other kind (non-straddle-type) is with both O-H bond hydrogen-bonded and the dipole vector point away from the liquid phase. For straddle-type interfacial water molecule, both the free O-H bond and the hydrogen-bonded O-H bond can only be treated as \( C_{\infty v} \) symmetry vibrationally. While the non-straddle-type water molecule belongs to the \( C_{2v} \) symmetry. The vibrational spectra of the stretching modes of both types of interfacial water molecules have been identified and the molecular orientation has been studied.

However, it is that the electronic transitions are responsible for the SHG responses. Electronically, it is expected that the straddle-type water molecule should still possesses most signature of \( C_{2v} \) symmetry, because the hydrogen bonding to one of the O-H bond perturbs much less significantly to the electronic transition, which has much higher transition energy and much broader spectra, than to the vibrational transition. Therefore, it is easy to conclude that the straddle-type water molecule should give very small SHG signal, with the dipole vector almost parallel to the interface. Du et al. have shown that the straddle-type water molecule consists about 20% of the interfacial water molecules at the neat air/water interface. Thus, it is easy to see that the SHG signal comes almost all from the non-straddle-type water molecule. So, the \( D \) values determined in Section IV.B above provide orientational information only for the non-straddle-type water molecule at the neat air/water inter-
face. The orientational parameter $D$ obtained above indicated that the dipole vector of the non-straddle-type interfacial water molecule oriented around an apparent orientational angle of $40^\circ$ from the interface normal. However, this angle was calculated assuming a $\delta$ distribution function of the tilt angle $\theta$. As Simpson and Rowlen have shown, such an orientational angle is close to the ‘Magic Angle’ $\theta = 39.2^\circ$. Therefore, it may come from a relatively broad orientational distribution. Indeed, because there are different kinds of non-straddle-type water molecule at the interface region, as clearly indicated by the broad vibrational spectra between $3100\text{cm}^{-1}$ and $3500\text{cm}^{-1}$ in SFG- VS studies, a relatively broad orientational distribution for the non-straddle-type hydrogen-bonded water molecule is generally expected. However, the distribution width should not be extremely broad. Otherwise, SHG or SFG-VS signal from the air/water interface should have been too weak to be detectable. On the other hand, recent detailed SFG-VS analysis has demonstrated that the orientational distribution of straddle-type water molecule appears to be as narrower as less than $15^\circ$.67,68

On the other hand, broad orientational distribution has been predicted for both the straddle-type and non-straddle-type interfacial water molecule from Molecular Dynamics (MD) and Monte Carlo (MC) simulation studies.71,72,73,74,75,76,77,78,79,80,81,82,83 Sokhan and Tildesley discussed the apparent disagreement of the early SHG and SFG results for the neat air/water interface structure.87,88 Goh et al.’s early SHG studies indicated that water hydrogens are pointing towards the liquid side.2 While Du et al.’s SFG-VS study identified the staddle-type water molecule at the interface. From their simulation results, Sokhan and Tildesley believed that SHG and SFG-VS techniques are sensitive to different parts of the interface, respectively. Simulation results often found that the plane of water molecule is aligned approximately parallel to the interface on the liquid side and perpendicular to the interface on the gas side, and the dominant contribution to the interface susceptibility is from the liquid side.72,73,74,75,76,77,78,79,80,81,82 Unfortunately, such conclusions are drastically in disagreement with known SHG and SFG-VS experimental observations of the neat air/water interface, because when the water molecule has its molecular plane lying parallel to the interface, it is impossible to detect any SHG or SFG-VS signal in any polarization and experimental configuration. Detailed analysis of the SHG and SFG-VS experimental data has been significantly improved and systematically demonstrated in recent years.33,44,55,67,68,83,84,85,86,87,88,89,90,91

Even though simulation results have provided a great deal of detailed understandings of the liquid interfaces, these disagreements between experimental and theoretical results suggest that the physical picture provided by the simulations may need to be systematically reexamined as discussed below. As we have demonstrated above, SHG probes mainly the non-straddle-type of interfacial water molecule, which has both O-H bond hydrogen-bonded. On the other hand, SFG-VS probes the stretching vibrational spectra of both the straddle-type and the non-straddle-type interfacial molecules.26,65,66,67,68 Recent detailed analysis of the SFG-VS spectra in different polarizations and experimental configurations have helped to clarify the spectral assignments, symmetry determination of the interfacial water species, as well as understanding more on the orientation and motion of water molecules at the neat air/water interface.27,68 It has been known that most of these non-straddle-type water molecules have either 4 or 3 hydrogen-bonds on average.65,66,67,68,69,71 Therefore, these non-straddle-type water molecules have to reside on the liquid side instead of the gas side as suggested by the simulation results. As probed by SHG and SFG-VS, their molecular plane can not be close to parallel to the interface. Of course, it is clear that the straddle-type water molecule is at the outermost edge of the liquid boundary, and its molecular plane is certainly close to perpendicular to the liquid interface. However, to call this layer as the gas side of the interface may not be appropriate, because the air/water interface is extremely sharp (3.2Å) from X-ray reflectivity22,93 and theoretical simulations.21,94 As the experimental analyses have consistently given relatively narrower orientational distribution of the liquid interfacial molecules, simulation results have always accounted for a much broader orientational distribution.82,86,87,89,90,91,93,96,97 Such issue has to be answered in the future studies.

Here we make one final comment on the orientational energy of the air/water interface. Using the temperature effect of SHG signal they measured, Goh et al. concluded that it is about $1/kT$, which suggested a quite disordered air/water interface at the room temperature. Since now the temperature effect has to be gone, the value of the orientational energy from the same treatment of Goh et al. has to be much bigger than a few $kT$. This nevertheless suggests a much better ordered air/water interface, and it is consistent with the hydrogen-bonding nature of the molecules at the neat air/water interface.88 The hydrogen bond energy is typically about 5kcal/mol, and it implies a much well ordered interface structure. In short conclusion, non-resonant SHG provides orientational measurement of the non-straddle-type of interfacial water molecule. Its dipole vector orientation is distributed around $40^\circ$ from the interface normal. This picture is fully consistent with and complementary to the SFG-VS experimental results. Molecular simulation results may need to be reexamined for detailed orientational structure of the neat air/water interface.

V. CONCLUSION

As Shen had insightfully pointed out, the major obstacle in the advance of the (SHG) technique for surface studies is the lack of microscopic understanding of the
surface nonlinear susceptibility \( \chi^1 \). However, the over simplifying uniaxial molecular model has been generally used in the field. In recent years, efforts for systematic treatment of the problem beyond the uniaxial molecular model have been attempted by Simpson and co-workers. Our recent experiences in quantitative treatment of the SFG-VS spectra, which always involves treatment of non-uniaxial molecular groups, prompted us to work similarly on the treatment of SHG of molecular interfaces.

In this work, we re-examined the problem of the SHG reflected from neat air/water interface with detailed treatment on the connection between the microscopic polarizability of water molecule and macroscopic susceptibility of the interface. Because these treatment on microscopic polarizability is based on the molecular symmetry properties of single water molecule, so it can be well suitable for treating water molecule, as well as other molecules with the same symmetry, at different molecular interfaces. After examination on issues of the origin and validity of the Kleinman symmetry, we have concluded that the broken of macroscopic Kleinman symmetry of the neat air/water interface is not an indication for quadrupole (bulk) contribution to the surface SHG signal, as previous studies suggested and generally believed in the field. We further demonstrated that using dipole contribution only can fully address the broken of macroscopic Kleinman symmetry of the air/water interface. Using properly combined molecular polarizability tensor terms, we further simplified the treatment and are able to obtain the value of orientational parameter \( D \) from SHG data. Such procedures can be generally transferred to the treatment of interfacial molecules belong to different molecular symmetry.

In conclusion, the SHG signal from the neat air/water interface can be treated fully with dipole (local or interface) contribution. The broken of macroscopic Kleinman symmetry is not a sufficient condition for quadrupole (nonlocal or bulk) contributions in surface SHG. Even though in general the quadrupole (bulk) contributions has to be considered in SHG studies, this work suggests that they can be very small or even negligible for the neat air/water interface, which has long been considered the primary case favoring dominant quadrupole contributions. The successful treatment of the neat air/water interface with dipole contribution terms indicates that SHG probably is indeed a probe of the surfaces and interfaces of isotropic fluids, as strongly argued by Andrews et al. The treatment and approaches we presented here can be applied and tested with other fluid interfaces.

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