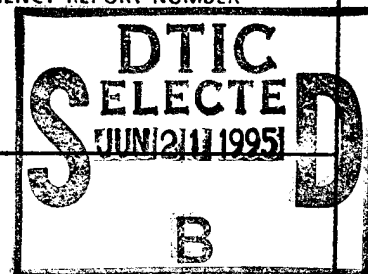


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Studies of the n-Alkane/Water Interface by Total Internal Reflection Second Harmonic Generation

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Abstract:

Total internal reflection second harmonic generation (TIRSHG) has made possible the study of a series of neat n-alkane/water interfaces. Analysis of the incident and polarization angular dependent SH response allows for determination of interfacial nonlinear molecular properties. The measured surface nonlinear susceptibilities may be indicative of a high degree of interfacial order.

We report the first use of total internal reflection second harmonic generation (TIRSHG) at an oil/water interface. Due to the surface specificity of SHG this technique has been used extensively in the past to study a number of interfaces[1-6]. By utilizing a total internal reflection geometry the SH response from a series of neat n-alkane/water interfaces has been found to be enhanced by several orders of magnitude. The results show excellent agreement with theoretical predictions of the angular and polarization dependence of the nonlinear response. The successful demonstration of the enhancement greatly expands the capabilities of SHG to study a variety of interfaces between two immiscible liquids. Under an external reflection geometry, the SH polarizability of the oil/water interface is often too low to allow measurement of interfacial molecular parameters unless a probe molecule is placed at the interface which is resonant with either the fundamental or SH frequency.[7-9]

The enhanced SH response under TIR has been explained theoretically by Bloembergen and Pershan, Dick *et al*, and others.[10-15] At the critical angle when the incident light field is totally reflected at the interface between two insulators an evanescent wave propagates in the interfacial region; the evanescent wave decaying exponentially into the medium of lower index of refraction. In linear optics the sum of the transmitted and reflected field amplitudes is a constant even under TIR. However, the nonlinear response under total reflection can be enhanced considerably because the evanescent wave propagating within the interfacial region gives rise to a SH field which can exceed that from an external reflection geometry. This is due to the increased phase matching of the evanescent wave in the nonlinear interfacial region.[16] Theoretically two orders of magnitude intensity increase in the SH response at the critical angle should be observed over that of an external reflection geometry.[13]

Experimentally a cylindrical quartz cell was employed for the TIRSHG studies. All the liquids used (decane, nonane, and octane purchased from Aldrich and ultrapure water) were passed through a 1.0 μm filter prior to use. The optical cell was open to the atmosphere to avoid changes in the interfacial tension due to thermal fluctuations. The SH experiments were performed with the 532nm second harmonic output of a Q-switched Nd:YAG laser. (10nsec pulses of 2-5mJ, at a repetition rate of 10Hz were employed.) The 532nm incident beam was collimated to a diameter of 0.25-0.5mm and directed onto the interface from the high index of refraction side (n-alkane). The input polarization was controlled by a half-waveplate. The reflected SH at 266nm was passed through an output polarizer, a monochromator, and detected with a PMT. Gated electronics were used for SH signal collection.

Since the liquid/liquid interface is rotationally invariant about the surface normal there are only three non vanishing elements of the surface nonlinear susceptibility tensor, $\chi^{(2)}$, namely χ_{zzz} , χ_{zii} , and χ_{izi} where ($i = x,y$). The theoretical expressions for the SH intensity for the relevant polarization combinations being:

$$I_{M_{in},S_{out}}^{2\omega} \propto |f_y f_z \hat{f}_y \chi_{iiz}|^2 \quad (1)$$

$$I_{S_{in},P_{out}}^{2\omega} \propto |f_y^2 \hat{f}_z \chi_{zii}|^2 \quad (2)$$

$$I_{P_{in},P_{out}}^{2\omega} \propto |f_x f_z \hat{f}_x \chi_{iiz} + f_x^2 \hat{f}_z \chi_{zii} + f_z^2 \hat{f}_z \chi_{zzz}|^2 \quad (3)$$

where f 's are the linear and \hat{f} 's are the nonlinear Fresnel factors which are dependent upon the incident angle (θ) and the polarization angle (γ) of the fundamental light field. The coordinates are defined such that y is perpendicular to the plane of incidence and x and z lie in the plane.

The SH response as a function of input polarization angle (γ) for the decane/water interface is shown in Figure 1(a) and 1(b) for S and P output polarizations respectively. Both graphs contain data at two incident angles, 64° and 72° . The order of magnitude increase in the signal at an incident angle of 72° relative to 64° corresponds to the total reflection of the fundamental light field near the critical angle. Figure 1(a) has maxima at $\gamma = 45^\circ, 135^\circ, \dots$ which satisfy the symmetry requirements of Equation (1). The maximum intensities at these angles, which correspond to M_{in} polarization, can be used to determine the absolute value of χ_{izi}^{eff} . This observation can be also used to accurately assign the detected signal to the SH response since no other linear or nonlinear scattering process can reproduce the observed polarization dependence. The minima in Figure 1(b) at $\gamma = 90^\circ, 270^\circ \dots$ correspond to S_{in} polarization and maxima at $\gamma = 0^\circ, 180^\circ \dots$ to P_{in} polarization. The SH intensity at the minima and maxima in Figure 1(b) can be used to derive χ_{zii}^{eff} and χ_{zzz}^{eff} respectively.

The measured ratios of the effective surface nonlinear susceptibility elements for the decane/water interface are; $\chi_{zzz}^{eff}/\chi_{zii}^{eff} = 2.2 \pm 0.4$ and $\chi_{zzz}^{eff}/\chi_{izi}^{eff} = 2.1 \pm 0.3$. This results in a ratio of $\chi_{izi}^{eff}/\chi_{zii}^{eff}$ of 0.97. According to the Kleinman symmetry rule, under the dipole approximation and at wavelengths far from resonance, χ_{zii} and χ_{izi} are equal.[17] This suggests that the observed SH signal for decane/water is arising predominately from a dipolar response which is usually considered to be indicative of a

high degree of interfacial ordering. If the interfacial region is highly disordered one would expect a much larger contribution from multipolar terms. This result can be compared with studies done at the water/air interface where $\chi_{izi}^{eff}/\chi_{zii}^{eff} = 2.3$. [18,19] In this study it was determined that the large value from the water/air interface is due to a large contribution from multipolar terms. Our observation, which suggests that the interface possesses Kleinman symmetry, is consistent with recent molecular dynamics calculations of the decane/water interface. [20] These studies suggest that the hydrocarbon chains are horizontally ordered with respect to the interface with the water dipoles pointing away from the interface. A similar value for $\chi_{izi}^{eff}/\chi_{zii}^{eff}$ is obtained for octane/water (0.95 ± 0.1) whereas the value for nonane/water is measurably lower at 0.69 ± 0.08 . That these measured values are different is somewhat surprising given the similar nonpolar structure of the n-alkanes. Further studies of a broad range of alkanes are currently in progress in this laboratory.

Figures 2(a), (b) and (c) show the SH dependence on the fundamental incident angle (θ) for the decane/water, nonane/water and octane/water interfaces. Data and theoretical curves are shown for the P_{in}, P_{out} polarization combination. All data were fit from Equation (3) with a single adjustable parameter, the effective surface nonlinear susceptibility, χ_{zzz}^{eff} . The elements χ_{izi}^{eff} and χ_{zii}^{eff} were obtained by experimental fits to equations (1) and (2) respectively. The observed intensity is seen to agree very well with the theoretically calculated response from Equation (3). The SH intensity, as described in Equation (3), is dependent upon the linear transmission Fresnel coefficients for the fundamental field, a nonlinear Fresnel factor for the generated field at 2ω , and the experimentally calculated χ^{eff} values. The linear and nonlinear expressions, which include the dielectric constants of the bulk liquids, have maxima at the critical angles of the fundamental and SH frequencies, which corresponds to the two maxima of 70.6° and 75.7° . It should be noted that the bimodal behavior seen in Figure 2 is completely dependent upon the dispersion in the lower index water phase.

This is the first observation of such bimodal behavior in the observed angular dependent response. This behavior has been predicted theoretically.[13] That it has not been observed in previous studies of solid/air interfaces [21] is a consequence of the low dispersion in air relative to bulk liquids. The peaks of the curves in Figure 2 shift to larger angles as one proceeds down the alkane series, C₁₀, C₉, and C₈. This trend results from a decrease in the index of refraction at both the fundamental and SH frequencies due to the decreasing carbon chain length. The change in the index of refraction also explains the relative change in the peak intensities at θ_c^ω and $\theta_c^{2\omega}$. As the index of the n-alkane decrease the relative difference between θ_c^ω and $\theta_c^{2\omega}$ increases. This increased separations can be seen mathematically as a deconvolution of the linear, f , and nonlinear, f^2 , field contribution in Equation (1, 2 and 3).

We have demonstrated for the first time the value of employing TIRSHG to study oil/water interfaces. The polarization and angular dependent SH response from a series of n-alkane interfaces have been examined and agree well with established theory. By utilizing TIRSHG the effective surface nonlinear susceptibilities for decane/water, nonane/water, and octane/water were determined from polarization measurements. The ratio of $\chi_{izi}^{eff}/\chi_{zii}^{eff}$ for decane/water and octane/water suggests the interfaces possesses Kleinman symmetry and may be highly ordered. The results obtained for nonane/water suggest a reduction in the interfacial order as seen in the deviation of the ratio $\chi_{izi}^{eff}/\chi_{zii}^{eff}$ from unity. The correlation between the surface susceptibilities and interfacial or molecular order is under current investigation. The angular dependent SH data clearly shows the effect on the observed SH response due to the optical dispersion in the bulk liquids, in particular water. The successful demonstration of the enhancement attainable with TIRSHG greatly expands the capability of SHG in the study of liquid-liquid interfaces. The use of total internal reflection SHG at the liquid-liquid junction provides a means by which the properties and processes of interfaces can be studied directly without the need for resonant enhanced SHG. This unique geometry helps to alleviate

photochemical decomposition and thermal heating problems which arose in our earlier studies under external reflection.

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References.

1. Y.R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
2. G.L. Richmond, J.M. Robinson and V.L. Shannon, *Prog. Surf. Sci.*, **28**, 1 (1988).
3. K.B. Eisenthal, *Acc. Chem. Res.*, **26**, 636 (1993).
4. R.M. Corn, *Anal. Chem.*, **63**, 285A (1991).
5. T.F. Heinz, in *Nonlinear Surface Electromagnetic Phenomena*, H.E. Ponath and G.I. Stegeman, eds. (Elsevier, Amsterdam, 1991) p. 353.
6. Y.R. Shen, *Nature*, **337**, 519 (1989).
7. D.A. Higgins and R.M. Corn, *J. Phys. Chem*, **97**, 489 (1993).
8. D.A. Higgins, R.R. Naujok and R.M. Corn, *Chem. Phys. Lett.*, **213**, 485 (1993).
9. S.G. Grubb, M.W. Kim, T. Rasing and Y.R. Shen, *Langmuir* **4**, 452 (1988).
10. N. Bloembergen and P.S. Pershan, *Phys. Rev.* **128**, 606 (1962).
11. N. Bloembergen, *Opt Acta.*, **13**, 311 (1966).
12. N. Bloembergen, H.J. Simmon, and C.H. Lee, *Phys. Rev.*, **181**, 1261 (1969).
13. B. Dick, A. Gierulski and G. Marowsky, *Appl. Phys. B*, **42**, 237 (1987).
14. P. Guyot-Sionnest and Y.R. Shen, *Appl. Phys. B*, **42**, 237 (1987).
15. B.U. Felderhof and G. Marowsky, *Appl. Phys. B*, **44**, 11 (1987).
16. J.M. Vigouteux and D. Courjon, *J. Mod. Opt.*, **36**, 1575 (1989).
17. D.A. Kleinman, *Phys. Rev.*, **126**, 1977 (1962).
18. M.C. Goh, J.M. Hicks, K. Kennitz, G.R. Pinto, K. Bhattacharyya, K.B. Eisenthal, and T.F. Heinz, *J. Phys. Chem.*, **92**, 5074 (1988).
19. M.C. Goh and K.B. Eisenthal, *Chem. Phys. Lett.*, **157**, 101 (1989).

20. A.R. van Buuren, S-J. Marrink, and H.J.C. Berendsen, J. Phys. Chem., **97**, 9206 (1993).
21. B.U. Felderhof, A. Bratz, G. Marowsky, O. Roders and F. Sieverdes, J. Opt. Soc. Am. B, **10**, 1824 (1993).

Figure Captions.

Figure 1. SH intensity verses input polarization angle (γ) for (a) S_{out} and (b) P_{out} polarization for decane/water. Two incident angles (θ) are shown, $\theta=64^\circ$ (C) and $\theta=72^\circ$ (\bullet). A large increase in the SH intensity is seen near the critical angle, $\theta=72^\circ$ compared to $\theta=64^\circ$.

Figure 2. SH intensity (P_{in} , P_{out}) verses incident angle (θ) for (a) decane/water, (b) nonane/water, and (c) octane/water interfaces. The maxima at (a) 70.6° , (b) 71.6° , and (c) 72.6° correspond to θ_c^ω and those at (a) 75.7° , (b) 76.8° , and (c) 78.3° to $\theta_c^{2\omega}$.