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# THE ENERGETICS OF ORIENTATION AT THE LIQUID–VAPOR INTERFACE OF WATER

M. Cynthia GOH and Kenneth B. EISENTHAL
*Department of Chemistry, Columbia University, New York, NY 10027, USA*

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To study the energetics of orientation of water molecules at the neat liquid–vapor interface of water, the temperature dependence of the second harmonic signal is examined. With the use of a simple model, an energy of orientation at the neat liquid–vapor interface is estimated to be about $\frac{1}{3}kT$ at room temperature. We discuss the role of hydrogen bonding and the permanent moments of water on its molecular orientation at the interface.

## 1. Introduction

The technique of second harmonic generation (SHG) has been recently employed in a variety of studies regarding surfaces [1–14]. In this approach, light of frequency $\omega$ impinges upon the surface, which can then radiate coherently at $2\omega$ through the second-order nonlinear susceptibility, $\chi_{ijk}$, which describes the nonlinear response of the surface to the driving incoming fields $E_j$ and $E_k$ at the frequency $\omega$,

$$P_i(2\omega)=\chi_{ijk}E_j(\omega)\,E_k(\omega)\,, \qquad (1)$$

where $P_i$ is the polarization at $2\omega$ in the $i$ direction. In the simplest case, that of a uniaxial molecule in the absence of local fields, the second-order susceptibilities, $\chi_{ijk}$, are related to the single dipole molecular hyperpolarizability, $\alpha_{\xi\xi\xi}$, in a simple manner [3],

$$\chi_{ZZZ}=N_s\langle\cos^3\theta\rangle\alpha_{\xi\xi\xi}\,, \qquad (2)$$

$$\chi_{XZX}=\chi_{ZXX}=N_s\langle\cos\theta\,\sin^2\theta\rangle\alpha_{\xi\xi\xi}\,, \qquad (3)$$

where $N_s$ is the number of surface molecules per cm$^2$, $\theta$ is the angle between the molecular axis $\xi$ and the laboratory frame, and $\langle\;\rangle$ denotes orientational averaging.

Recently we have used SHG to measure the three nonvanishing susceptibilities for the water surface, $\chi_{ZZZ}$, $\chi_{ZXX}$ and $\chi_{XZX}$ [14]. We pointed out that in order to interpret the SH signal from water, two complicating issues must be addressed. The first is due to the fact that water is not a uniaxial molecule and thus more than the one nonlinear polarizability element $\alpha_{\xi\xi\xi}$ must be considered. The second issue is the possible contribution of quadrupole in addition to dipole terms to the nonlinear susceptibility. The first problem we addressed by deriving expressions equivalent to (2) and (3) applicable to biaxial molecules [15]. The second problem is harder to address, and quite possibly very important. For instance, the Kleinmann symmetry rule [16] for dipolar susceptibilities states that in the static limit, $\chi_{XZX}$ and $\chi_{ZXX}$ should be equal; we noted that for water at room temperature, the measured $\chi_{XZX}$ is about twice $\chi_{ZXX}$, possibly due to quadrupolar contributions. We thus made an attempt to separate the dipolar contribution by a measurement of the temperature dependence of the effective susceptibilities [14]. We argued qualitatively that since the dipolar susceptibility is sensitive to the absolute orientation of molecules, that is, up versus down, and since the effect of increasing temperature is to randomize this orientational distribution, then any dipolar contribution must be strongly temperature-dependent relative to a quadrupolar term. With this argument we concluded that there is a substantial dipolar contribution to all the effective $\chi$'s of water at room temperature. From the dipolar contribution we inferred the net absolute orientation at the surface. In this Letter we shall further examine the temperature-dependent SH signal with regard to the dipole part of the susceptibilities, and present a simple model that

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allows us to evaluate the energy that leads to a net absolute orientation at the surface.

## 2. The source of SHG

In order to understand the behavior of the nonlinear susceptibility with temperature, we first have to determine the source of the measured SH signal for the water surface. While SHG is forbidden in isotropic bulk media in the electric dipole approximation, there could exist bulk contributions through higher-order terms such as the electric quadrupole and magnetic dipole transitions [1,17,18]. Bloembergen et al. [17] have derived an expression for such, which shows that bulk contributions are purely p-polarized and thus do not contribute to the generated s-polarized SH radiation. In addition, since the bulk fluid is isotropic, any orientational averaging must be independent of temperature, and thus it may be argued that bulk contributions to the SH signal must be temperature-independent. Hence, in our examination of the temperature-dependent nonlinear susceptibilities, we need not worry about the possible bulk quadrupole contributions since they do not change with temperature. However, there could also be higher-order terms from surface sources [17]. It has previously been shown that the surface SH may be described in terms of an effective susceptibility that consists of electric dipole, electric quadrupole and magnetic dipole terms [18]. Furthermore, by subdividing the interface into layers in the $Z$-direction, an expression for the effective $\chi_{XZX}$ has been derived [18,19]; the other susceptibility elements may be treated similarly. In any of these cases, however, the quadrupole contribution is not simple to evaluate. In section 3 we shall examine the temperature behavior of the dipolar susceptibility, based on the approximation that it is the dominant term, and, with a model of the interface, fit it to our experimental data.

## 3. Energetics

We have argued that the strong temperature dependence of $\chi_{ZXX}$ indicates the presence of a substantial contribution from the dipolar $\chi_{ZXX}$, and thus a net orientation at the interface. We would like to make an estimate of the energy involved in this by looking at how the SH signal decays with temperature. We note that a molecule at the interface sees a different environment above and below it due to the difference in the two bulk phases. We can thus discuss orientation at the surface in terms of the bulk phases giving rise to an effective field acting on an interface molecule. Since $\chi^{\mathrm{D}}$ is related to an odd moment, e.g. $\langle\cos^3\theta\rangle$, the fact that we get a SH signal indicates that the orienting field distinguishes between up versus down, and is therefore an odd function of $\theta$. If the probabilities of up versus down orientations were the same, then $\langle\cos^3\theta\rangle$ and $\chi^{\mathrm{D}}$ would be zero. We chose to begin with a simple interaction given by $W\cos\theta$, where $W$ is an energy of orientation, and $\theta$ is the angle between the field and a fixed axis on the molecule. Our picture of the molecules at the interface is thus similar to that of a system of permanent dipoles in an external field. We can then perform the orientational average,

$$\langle\cos\theta\sin^2\theta\rangle = \frac{\int_0^{2\pi}\cos\theta\sin^2\theta\exp(-W\cos\theta/kT)\sin\theta\,\mathrm{d}\theta}{\int_0^{2\pi}\exp(-W\cos\theta/kT)\sin\theta\,\mathrm{d}\theta}. \tag{4}$$

Evaluating (4) yields the temperature dependence of $\chi^{\mathrm{D}}_{ZXX}$ and $\chi^{\mathrm{D}}_{XZX}$, which is given by

$$\frac{6kT}{W}\coth\left(\frac{W}{kT}\right)-\frac{2kT}{W}-\frac{6(kT)^3}{W^3}. \tag{5}$$

As has been pointed out, water is not a uniaxial molecule; thus (5) is strictly not valid. We can instead use a result we have previously derived [14,15], $(\chi^{\mathrm{D}}_{ZZZ}+2\chi^{\mathrm{D}}_{ZXX})\propto\langle\cos\theta\rangle$. Due to the larger error bars at the present time in $\chi^{\mathrm{eff}}_{ZZZ}$, however, we choose to approximate water as uniaxial and use (5).

The data presented (fig. 1) are normalized to the value at room temperature (295 K). We found that the above expression (5) does not fit our data if we assume a constant value for $W$: the measured temperature dependence is much stronger than that predicted by the picture given. However, if we argue that what gives rise to a net orientation in the liquid–vapor interface is the asymmetry an interface molecule experiences due to the difference in its molecular interactions with the two coexisting phases, then it is

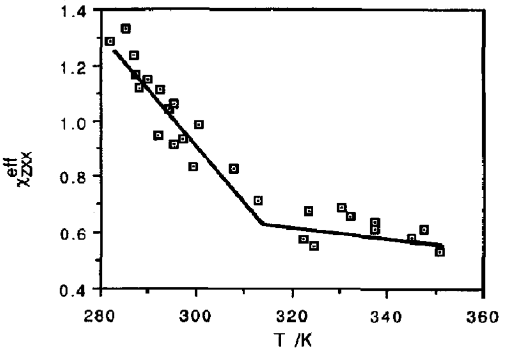

Fig. 1. The effective nonlinear susceptibility $\chi^{\rm eff}_{ZXX}$ as a function of temperature, normalized to its value at 295 K. The line is a two-parameter fit using (5) in the text.

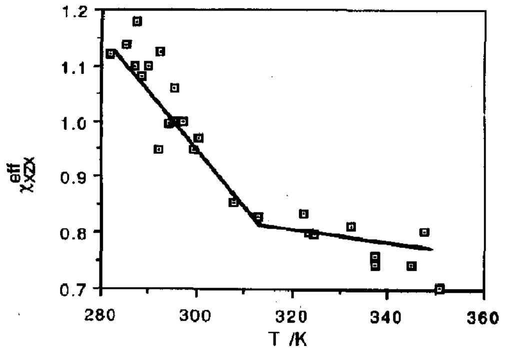

Fig. 2. The effective nonlinear susceptibility $\chi^{\rm eff}_{XZX}$ as a function of temperature normalized to its value at 295 K. The line is calculated using the fit for $\chi^{\rm eff}_{ZXX}$ as the dipolar part, in addition to a temperature-independent background term, possibly quadrupolar, that is 50% of the value of $\chi^{\rm eff}_{XZX}$ at 295 K.

reasonable to assume a temperature-dependent $W$, which should go to zero when the difference between the two phases disappears, i.e. at the critical point. However, a more important consideration, for water, is the existence of hydrogen bonding, which is known to play a significant role in producing structure in the bulk [20,21] and should therefore be taken into account in discussing orientation and structure at the surface. Since hydrogen bonding is strongly dependent on temperature, the energy of orientation, $W$, should be temperature-dependent. We thus postulate the following simple form

$$W=A\frac{T_0-T}{T_0}+B=A+B-\frac{A}{T_0}T, \qquad (6)$$

with $A=0$ for $T>T_0$. We can view $T_0$ in this description as the temperature at which the distortions or disruptions in the hydrogen-bonding network are large enough that H-bonding no longer contributes to the orientation of the interfacial water molecules. Near enough the liquid–vapor critical point we can also assume a temperature-dependent form for the second term, $B=B'[(T_c-T)/T_c]^{\beta}$, where $T_c$ is the critical temperature and $\beta$ is the critical exponent for the coexistence curve. In this experiment, water is far enough from its critical point, 647 K, that $B$ is approximately constant.

We used (6) to fit our data with two parameters using a nonlinear least-squares routine. In the case of $\chi_{ZXX}$ we are able to obtain a good fit (fig. 1) with $A=1600\pm130$ cal, $B=180\pm20$ cal and $T_0=315\pm10$ K. This translates to an energy of orientation of about 280±80 cal at 295 K. It is relevant to note that, based on various other experimental methods [21–24], significant distortion or disruption of hydrogen bonding in bulk water is thought to occur at about 340–350 K.

The $\chi_{XZX}$ data, unlike those of $\chi_{ZXX}$, cannot be fitted with the above model unless a temperature-independent background term (about 50% of the value at room temperature) is added to it. With this background term, the fit is shown in fig. 2. This background term can be ascribed to quadrupole contributions to the susceptibility, or possibly to the partial breakdown of the Kleinmann symmetry rules, since we are not strictly at $\omega=0$. However, we do not expect this latter effect to be large, since the frequencies of the light fields are far from the water resonances.

## 4. Discussion

With the simplifying assumptions we have made in our picture of orientation at the interface, we are able to examine the temperature-dependent SH signal in order to address important questions regarding the water surface. The strong temperature dependence of the SH signal is in accord with the existence of a nonnegligible dipolar susceptibility, and implies a significant amount of structure at the water surface at room temperature. In addition, a fraction of this structure decays rapidly with increasing temperature, well below the critical temperature of water (647 K), where the coexisting phases will become the same. This suggests that there are two different types of interactions giving rise to a net orientation at the water liquid–vapor interface, one of which is strongly temperature-dependent, and the other not. We ascribe the former to hydrogen bonding, and the latter to another, less temperature-dependent part, possibly the orientation due to the permanent moments of water. The net orientation at room temperature is due to both contributions. At temperatures higher than 40–50°C, absolute orientation due to hydrogen-bonding contributions become negligible. This, however, does not necessarily correspond to the breaking of all hydrogen bonds. Rather, we can picture this as a temperature at which enough bonds are broken, or distorted, such that the difference in energy of water molecules oriented up versus down due to hydrogen bonding becomes negligible. We are currently further pursuing this question of what leads to orientation at the neat liquid surface by extending our studies to other liquids: hydrogen-bonding liquids, non-hydrogen-bonding liquids with varying polarity and an ionic liquid.

## 5. Conclusion

We have measured the temperature dependence of the nonlinear susceptibility of neat water and related it to the energetics of orientation at the surface. The strong temperature-dependent decrease in the nonlinear susceptibility observed in the range of 280 to 320 K is attributed to the decay of hydrogen-bonding orientation forces in this range. The slower decay at higher temperatures is attributed to the orienting effects of permanent water moments. Using a simple model of the liquid–vapor interface, we estimate the energy that causes a net absolute orientation of water molecules at the interface to be about $\frac{1}{2}kT$ at room temperature.

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## References

[1] Y.R. Shen, Principles of nonlinear optics (Wiley, New York, 1984); J. Vacuum Sci. Technol. B 3 (1985) 1464.
[2] T.F. Heinz, C.K. Chen, D. Ricard and Y.R. Shen, Phys. Rev. Letters 48 (1982) 478.
[3] T.F. Heinz, H.W.K. Tom and Y.R. Shen, Phys. Rev. A 28 (1983) 1883.
[4] C.K. Chen, T.F. Heinz, D. Ricard and Y.R. Shen, Phys. Rev. B 27 (1983) 1965.
[5] G. Marowsky, A. Giersulsky and B. Dick, Opt. Commun. 52 (1985) 339.
[6] Th. Raising, Y.R. Shen, M.W. Kim, P. Valint and J. Bock, Phys. Rev. A 31 (1985) 537.
[7] Th. Raising, Y.R. Shen, M.W. Kim, S. Grubb and J. Bock, Phys. Rev. Letters 55 (1985) 2903.
[8] G. Richmond, Langmuir 2 (1986) 132.
[9] J.M. Hicks, K. Kemnitz, K.B. Eisenthal and T.F. Heinz, J. Phys. Chem. 90 (1986) 560.
[10] K. Kemnitz, K. Bhattacharyya, J.M. Hicks, G.R. Pinto, K.B. Eisenthal and T.F. Heinz, Chem. Phys. Letters 131 (1986) 285.
[11] K. Bhattacharyya, E.V. Sitzmann and K.B. Eisenthal, J. Chem. Phys. 87 (1987) 1442.
[12] K. Bhattacharyya, A. Castro, E.V. Sitzmann and K.B. Eisenthal, J. Chem. Phys. 89 (1988) 1.
[13] E.V. Sitzmann and K.B. Eisenthal, J. Phys. Chem. 92 (1988) 4579.
[14] M.C. Goh, J.M. Hicks, K. Kemnitz, G.R. Pinto, K. Bhattacharyya, K.B. Eisenthal and T.F. Heinz, J. Phys. Chem. 92 (1988) 5074.
[15] M.C. Goh, G.R. Pinto, K. Bhattacharyya, K.B. Eisenthal and T.F. Heinz, to be published.
[16] D.A. Kleinmann, Phys. Rev. 126 (1962) 1977.
[17] N. Bloembergen, R.K. Chang, S.S. Jha and C.H. Lee, Phys. Rev. 174 (1968) 813.
[18] P. Guyot-Sionnest and Y.R. Shen, Phys. Rev. B 35 (1987) 4420.
[19] P. Guyot-Sionnest, W. Chen and Y.R. Shen, Phys. Rev. B 33 (1986) 8254.
[20] F. Franks, Water, A comprehensive treatise, Vol. 1 (Plenum Press, New York, 1972).
[21] D. Eisenberg and W. Kauzmann, The structure and properties of water (Oxford Univ. Press, Oxford, 1969).
[22] G.E. Walrafen, M.R. Fisher, M.S. Hokmabadi and W.-H. Yang, J. Chem. Phys. 85 (1986) 6970.
[23] W.B. Monosmith and G.E. Walrafen, J. Chem. Phys. 81 (1984) 669.
[24] G. Walford and J.C. Dore, Mol. Phys. 34 (1977) 21.