Orientation Analysis

The theoretical framework of the orientation analysis in sum frequency generation is a well established procedure in the literature.[1-3] Below is the orientation analysis for the various water bonds where we consider that the this moiety is essentially isolated from the other water molecules. A diagram of the water molecule and the coordinates used is shown in Figure 1. The ratio of the different non-vanishing hyper-polarizability elements that are need in the orientation analysis are: for C_{2v} symmetric $\beta ccc/\beta aac=0.69$ and $\beta bbc/\beta aac=0.41$, and for and $C_{\infty v}$ vibration $\beta aac/\beta ccc=0.32$.[4, 5] The refractive index of the bulk phase of the water was set to: $n_2 sfg=1.337$, $n_2 vis=1.333$, and $n_2 ir=1.15$ while those of the interface were all set to 1.2.[6] In the case of the C_{2v} symmetry the twist angle ψ cannot be rotationally averaged thus the expression of the $\chi^{(2)}$ is a function of both twist ψ and tilt angle θ. For the symmetric stretch one obtains:

$$X^{(2)}_{xxz}=X^{(2)}_{yyz}=1/2<\cos\theta>(<\cos2\psi>\beta aac+<\sin2\psi>\beta bbc+\beta ccc))+1/2<\cos3\theta>(<\sin2\psi>\beta aac+<\cos2\psi>\beta bbc-\beta ccc);$$

$$X^{(2)}_{xzx}=X^{(2)}_{zxx}=X^{(2)}_{yzy}=X^{1}_{zyy}=-1/2(<\sin2\psi>\beta aac+<\cos2\psi>\beta bbc-\beta ccc)(<\cos\theta>-<\cos^3\theta>);$$

$$X^{(2)}_{zzz}=(<\sin2\psi>\beta aac+<\cos2\psi>\beta bbc)\cos\theta-(<\sin2\psi>\beta aac+<\cos2\psi>\beta bbc-\beta ccc)<\cos^3\theta>;$$

For the asymmetric stretch mode:

$$X^{(2)}_{xxz}=X^{(2)}_{yyz}=-\beta aca<\sin2\psi>(<\cos\theta>-<\cos^3\theta>);$$

$$X^{(2)}_{xzx}=X^{(2)}_{zxx}=X^{(2)}_{yzy}=X^{(2)}_{zyy}=-1/2\beta aca<\cos\theta>(<\cos^2\psi>-<\sin^2\psi>)+\beta aca<\sin2\psi><\cos3\theta>;$$

$$X^{(2)}_{zzz}=2\beta aca<\sin^2\psi>(<\cos\theta>-<\cos^3\theta>);$$

And finally for the $C_{\infty v}$ symmetry:

$$X^{(2)}_{xxz}=X^{(2)}_{yyz}=1/2\beta ccc(<\cos\theta>(\beta aac/\beta ccc)-1)-(1-(\beta aac/\beta ccc))<\cos^3\theta>;$$

$$X^{(2)}_{xzx}=X^{(2)}_{zxx}=X^{(2)}_{yzy}=X^{(2)}_{zyy}=1/2\beta ccc(1-(\beta aac/\beta ccc))(<\cos\theta>-<\cos^3>);$$

$$X^{(2)}_{zzz}=\beta ccc((\beta aac/\beta ccc)<\cos\theta>+(1-\beta aac/\beta ccc)(\cos^3\theta));$$

The number density of the interfacial molecules N was omitted in all equations for simplicity and the operator <> denotes orientational ensemble average over different molecular orientations.

Previous analysis[2, 3, 7] of the theoretical orientation of the water OH vibrations agrees with the theoretical plots showed below. These plots are only guides since they are based on a delta distribution of anngles, which is unlikely given the broad nature of the non hydrogen bonded region, however when a more realistic Gaussian distribution is assumed the plots showed similar tendencies.

The two water features `ice like´ and `liquid like´ have a clear symmetric character as the SSP polarization is always much stronger than the PPP and SPS. As the twist angle ψ decreases the PPP appears to be a little stronger than SPS, however both of them are much smaller than SSP.

The feature at 3560 cm^{-1} `the non donor OH bonds´ has a strong SPS and PPP signal and a small SSP one (see Figure 2a and Figure 6 of the paper). This indicates that the symmetric character is lost and a more asymmetric character is probable. For twist angles between 45 and 25 degrees the criteria are met only in the C_{2v} asymmetric vibration.
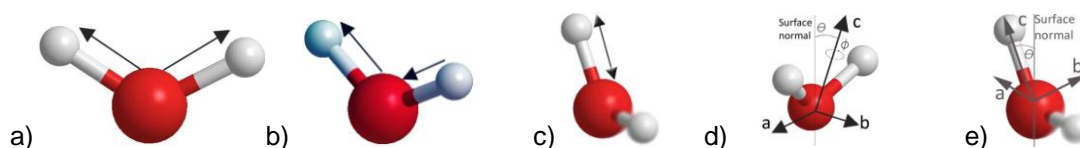

Figure 1. Molecular model for a) C_{2v} symmetric, b) C_{2v} asymmetric, c) $C_{\infty v}$, d) the Euler angles for the C_{2v} symmetry, and e) $C_{\infty v}$ symmetry coordinates.
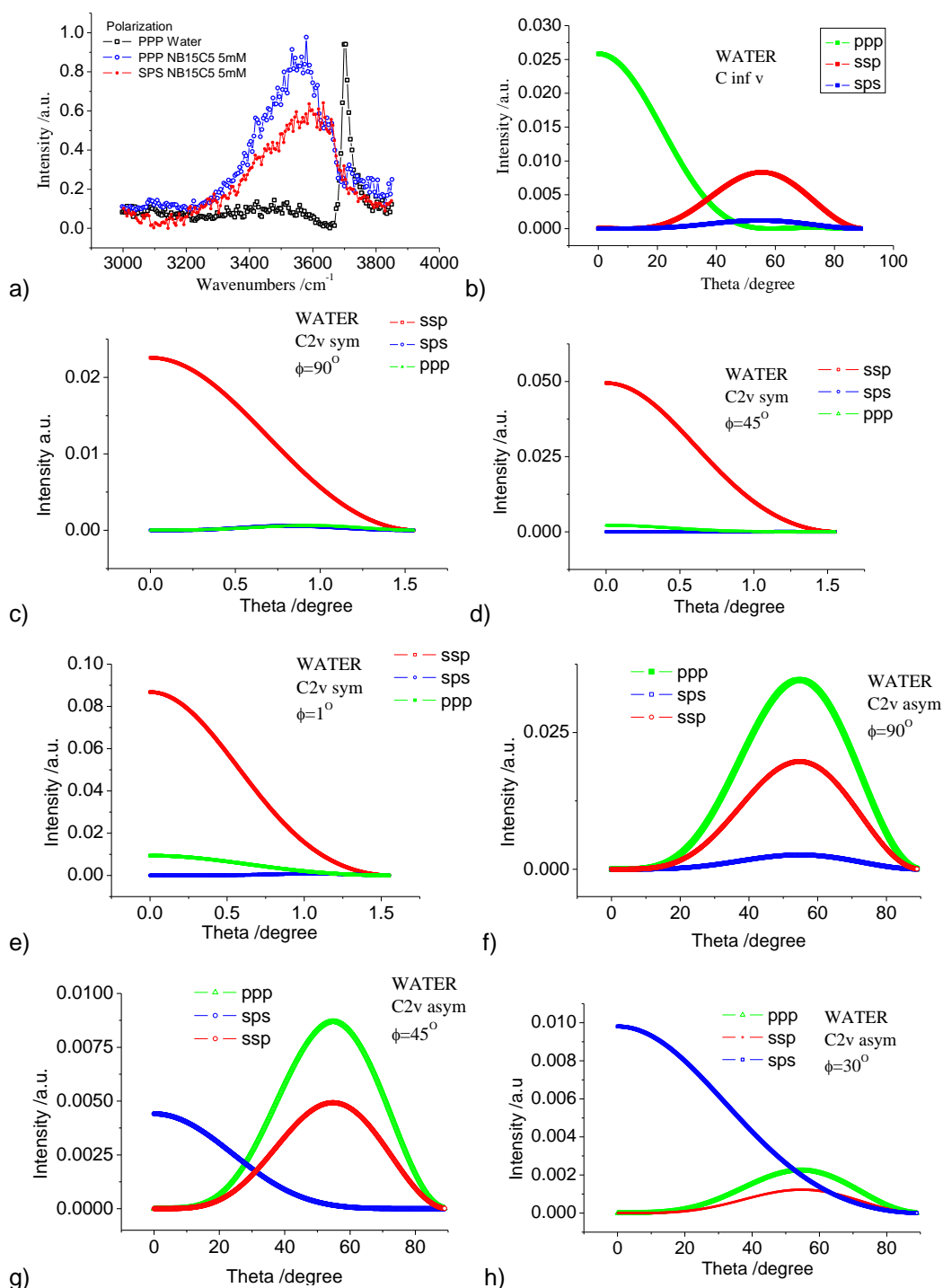
Figure 2. a)PPP and SPS polarization of the 5mM NB15C5 with the reference of PPP polarization of water. Calculated curves for the intensity of the three different polarization combination SSP, PPP and SPS for the OH stretch of water assuming: b) $C_{\infty v}$ symmetry, C_{2v} symmetry with ψ having c)90°, d)45°, e)1° for the symmetric stretch and f)90° g)45° and h)30° for the asymmetric stretch.

The net polar orientation of this water vibration cannot be directly obtained from the data since there is no phase data; however it can be inferred from the negative interference with the free OH band that they have the same phase. This and the fact that for the 45 to 25 twist, a tilt between 30 to 60 degrees is obtained, suggests that both H are directed upwards and thus hindered from participating in H bonding with the bulk water (The possibility of H bond acceptance thus remains). However, not all the solutions are physically reasonable. Larger tilt and twist angles would lead to one

of the hydrogens pointing downwards where it would most probably hydrogen bond with another water molecule – this would lead to the situation where the other hydrogen would have $C_{\infty v}$ symmetry.

The broad band that shows up around 3700 cm^{-1} (in the presence of a surface film) has a strong SSP signal and much smaller PPP and SPS contribution. This band has been observed by Tyrode, Richmond[8] and Du[9] before. The criterion set by the polarisation ratios is met by the C_{2v} and $C_{\infty v}$ symmetry types. The position of the band and the orientation analysis implies that the $C_{\infty v}$ vibration with tilt angles greater than 30 degree is more likely. Note that the c axis in this case is on the OH bond.

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