

# Computational methods

All MD simulations were performed at the classical level using LAMMPS. [1] The OPLS all-atom force field was used to represent PA molecules,[2, 3] while the TIP4P/2005 model was used for water.[4] Cross interactions between water and PA molecules were derived from Lorentz-Berthelot mixing rules. The simulations were carried out for a system containing two monolayers, with 36 fully protonated PA molecules each, placed at the opposite sides of a slab (along the z-direction) with 972 water molecules. This setup effectively reproduces the experimental conditions at  $\text{pH} = 5.6$ . [5] Two vacuum regions were placed above both monolayers to mimic the air interface. The initial coordinates were generated using PACKMOL.[6] After equilibration, the final structure was compressed/expanded in the lateral direction to change the area per monolayer while keeping the box dimension along the z-direction fixed. From these initial simulations, two different systems were prepared with surface area per molecule of  $19 \text{ \AA}^2$  and  $22 \text{ \AA}^2$ , corresponding to untilted and tilted phases, respectively. The present MD simulations with the OPLS force field predict a surface area per molecule for the untilted phase which is slightly smaller than the corresponding experimental value. However, it should be noted that the calculated surface pressure-area isotherm displays the same trend as the experimental one. This implies that the differences in surface area, which are common in MD simulations of monolayers and can be attributed to deficiencies in the force fields,[7] only shift the equilibrium between untilted and tilted phases but do not affect the underlying physics.

Both tilted and untilted phases of PA monolayers were equilibrated for 40 ns in the canonical (NVT: constant number of atoms, constant volume, constant temperature) ensemble. The temperature was maintained constant at 298 K using a global Nosé-Hoover thermostat with a relaxation time of 1 ps,[8, 9] and the equations of motion were integrated using the velocity Verlet algorithm with a timestep of 2 fs. The electrostatic interactions within  $9 \text{ \AA}$  were computed in real space using Coulomb's law, while the long-range contributions beyond this cutoff were calculated in reciprocal space using the particle-particle particle-mesh (PPPM) solver. After equilibration, 50 configurations for both tilted and untilted phases of the PA monolayers were extracted from the NVT trajectories and used in subsequent simulations to calculate the vSFG spectra of interfacial water. To directly probe the vibrational dynamics of the water OH stretches, the TIP4P/2005 model was replaced by the flexible q-TIP4P/F model which was shown to provide a reasonable description of the properties[10] and infrared spectrum[11] of liquid water. Consequently, a smaller timestep (0.5 fs) was used in these simulations to guarantee a proper integration of the equations of motion associated with the OH stretches. Each configuration was further equilibrated for 50 ps in the NVT ensemble, which were then followed by 100 ps in the micro-canonical (NVE: constant number of atoms, constant volume, constant energy) ensemble that were used to calculate the real and imaginary parts of the resonant second-order nonlinear susceptibility in the SSP polarization combination,

$\chi_{SSP}^{(2)}$ .

The calculation of  $\chi_{SSP}^{(2)}$  requires both dipole moments and polarizability tensors. Since these quantities are not accurately described by fixed-charge force fields as the q-TIP4P/F model,[11] they were both calculated using the MB- $\mu$  dipole moment and MB- $\alpha$  polarizability surfaces,[12, 13] which were developed along with the MB-pol many-body potential energy function.[14, 15, 16] It has been demonstrated that MB- $\mu$  and MB- $\alpha$  provide an accurate representation of the electrostatic properties of water and, when combined with MB-pol, enable an accurate modeling of the vibrational spectra from small water clusters[17] to liquid water[13], the air/water interface,[18] and ice.[19] Both real and imaginary parts of  $\chi_{SSP}^{(2)}$  were calculated using truncated cross-correlation functions, without including explicit short-range two-body contributions in the expressions of MB- $\mu$  and MB- $\alpha$ . This approximation was shown to provide an accurate approximation to the vSFG response of the air/water interface.[18] As discussed below, the convergence of  $\chi_{SSP}^{(2)}$  was obtained by including in the calculation of the corresponding response functions all water molecules within 4.6 Å of the Gibbs dividing surfaces. In the vSFG calculations, the alkyl chains of the PA molecules were truncated at the third carbon atom. It can be shown that this approximation leads to a significant reduction of the computational cost associated with the evaluation of both total dipole moment and polarizability without compromising the accuracy of the calculated vSFG response. To effectively take into account nuclear quantum effects, which are neglected in classical MD simulations,[18] the calculated  $\chi_{SSP}^{(2)}$  was redshifted by 152 cm<sup>-1</sup>, which is the frequency shift between the classical vSFG spectrum of liquid water predicted by q-TIP4P/F in the OH stretching region and the corresponding experimental spectrum.

To investigate possible third-order bulk contributions to the vSFG response,  $\chi_{SSP}^{(3)}$  for MB-pol was derived from the analogous quantity recently obtained for the charge response kernel (CRK) model.[20] Specifically, given the similarity between both real and imaginary components of  $\chi_{SSP}^{(2)}$  calculated for the air/water interface using the CRK and MB-pol models, [21, 18]  $\chi_{SSP}^{(3)}$  for MB-pol was estimated by scaling the corresponding CRK results by the intensity ratio of  $\chi_{SSP}^{(2)}$  calculated with the two models. For a complete description of the calculation of  $\chi_{SSP}^{(3)}$  with the CRK model, the interested reader is referred to Ref.20.

## References

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