Supplementary Information

Effects of Trimethylamine N-oxide and Urea on the Structure of Water at Liquid-Vapor Interfaces Studied Through Theoretical Vibrational Sum Frequency Generation Spectroscopy

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Table S1. Surface tension (γ) values for the interfacial systems of binary and ternary aqueous mixtures, along with the value for neat air-water interface.

System	γ **(mN/m)**
Neat air-water	55.847± 0.426
TMAO	62.650± 1.153
Urea	59.534± 0.445
TMAO:urea (1:1)	64.960± 0.528
TMAO:urea (1:2)	68.088± 0.689

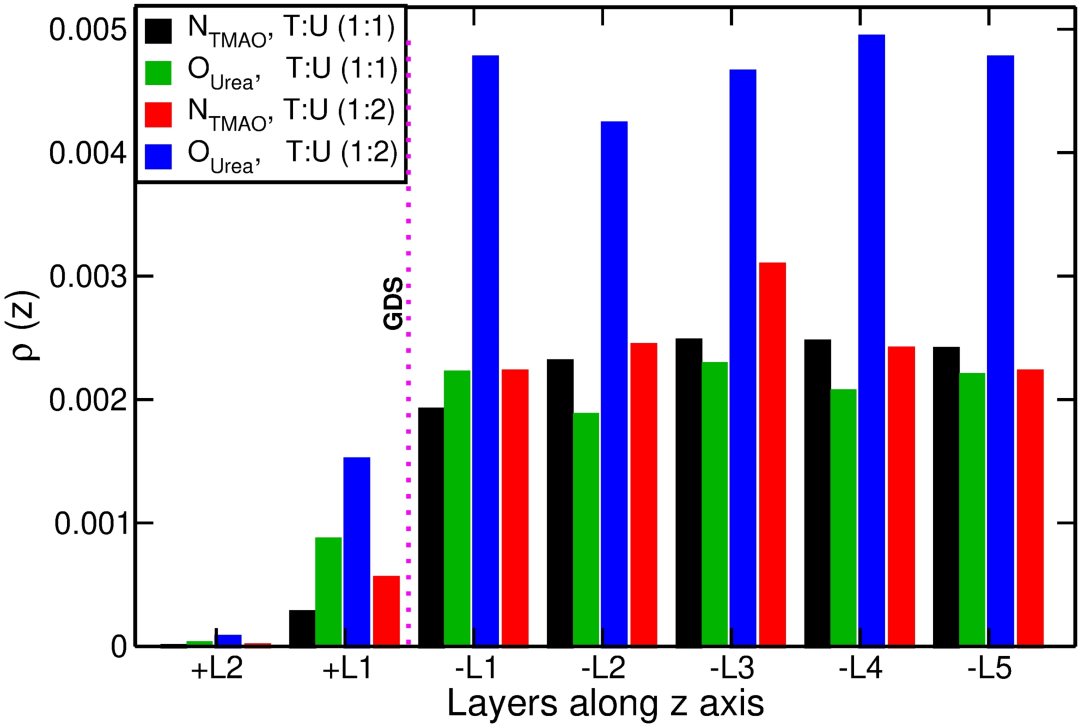

Figure S1: Number density profiles of the nitrogen atom of TMAO (N_{TMAO}) and the oxygen atom of urea (O_{Urea}) across different interfacial layers of thickness 2.5 Å in ternary aqueous mixtures. The Gibbs dividing surface (GDS) is located between layers +L1 and -L1, where +L1 and +L2 correspond to layers toward the vapor phase, and -L1, -L2..... correspond to layers toward the bulk phase.

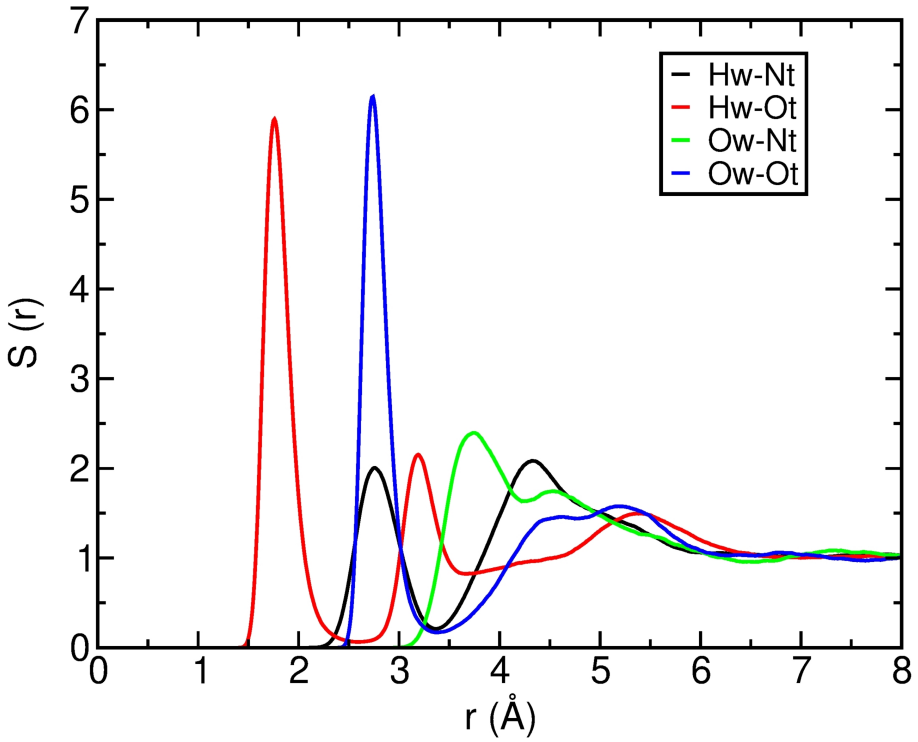

Figure S2: Slab radial distribution functions of the hydrogen (Hw) and oxygen (Ow) atoms of water with respect to the oxygen (Ot) and nitrogen (Nt) atoms of TMAO in the ternary TMAO:urea (1:1) aqueous mixture.

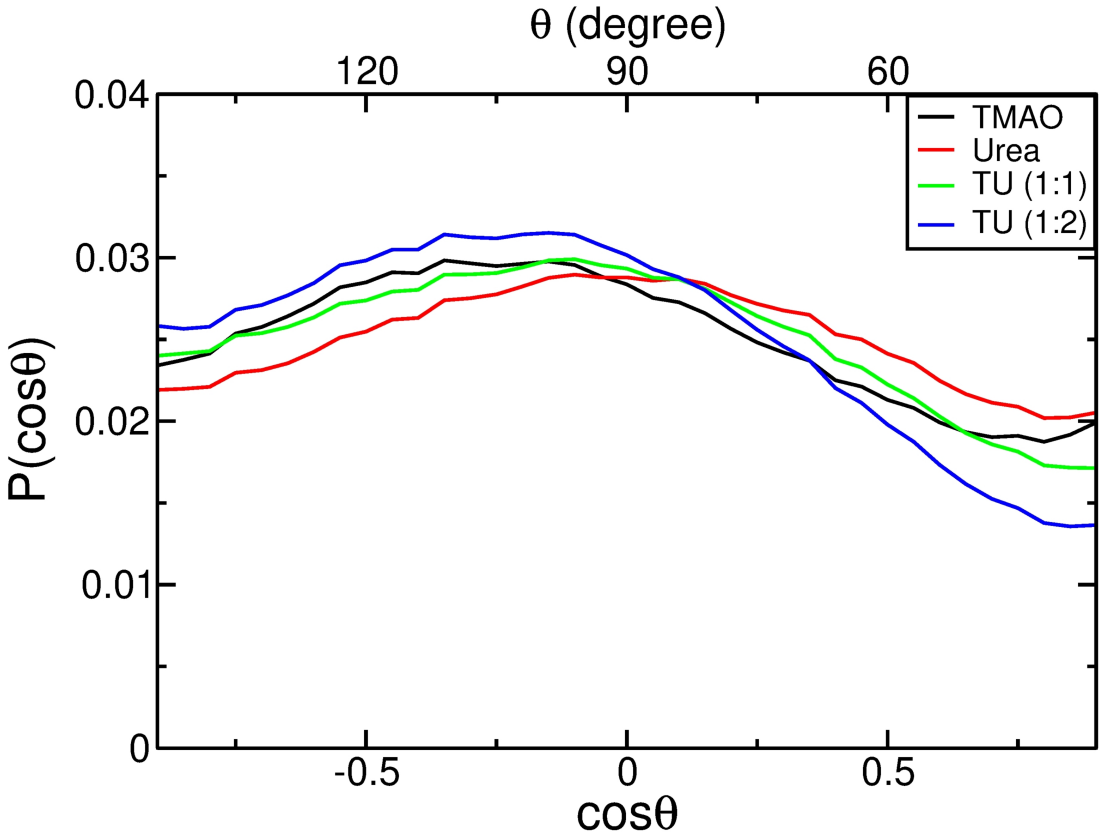

Figure S3: Orientational distributions of the OH vector of interfacial water with respect to the surface normal in the binary aqueous mixtures of TMAO and urea, and the ternary aqueous mixtures of TMAO: urea (1:1) and TMAO: urea (1:2).

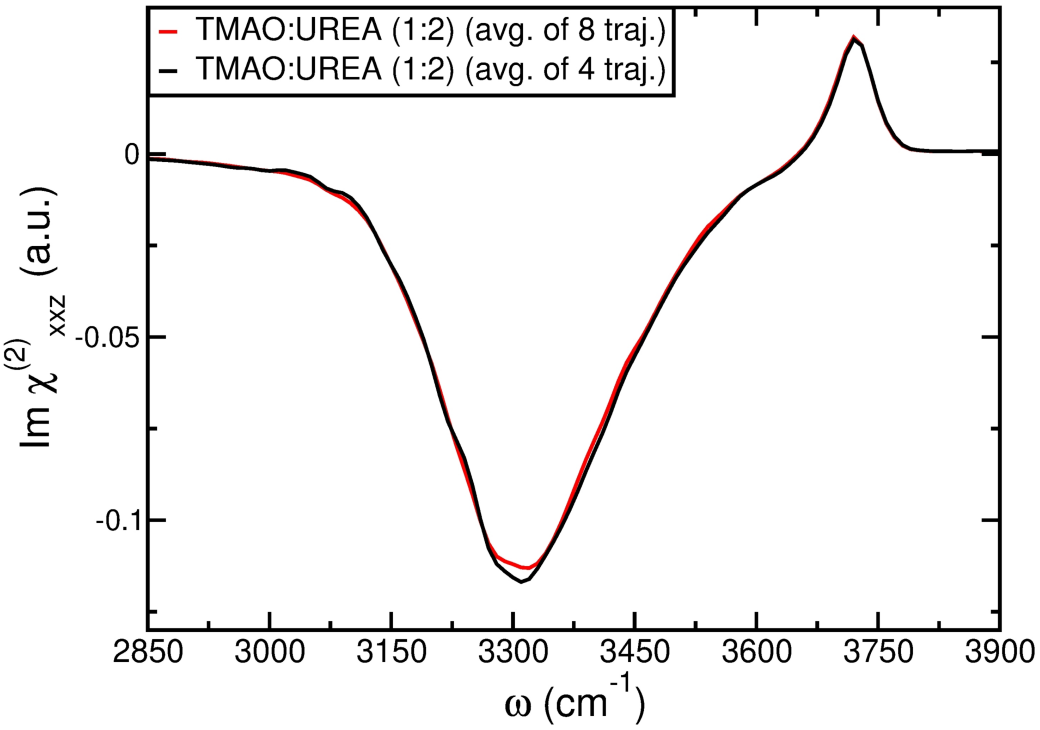

Figure S4: Total VSFG spectrum of the OH mode of water in the ternary TMAO:urea (1:2) aqueous mixture, averaged over four independent trajectories (black) and over eight independent trajectories (red).

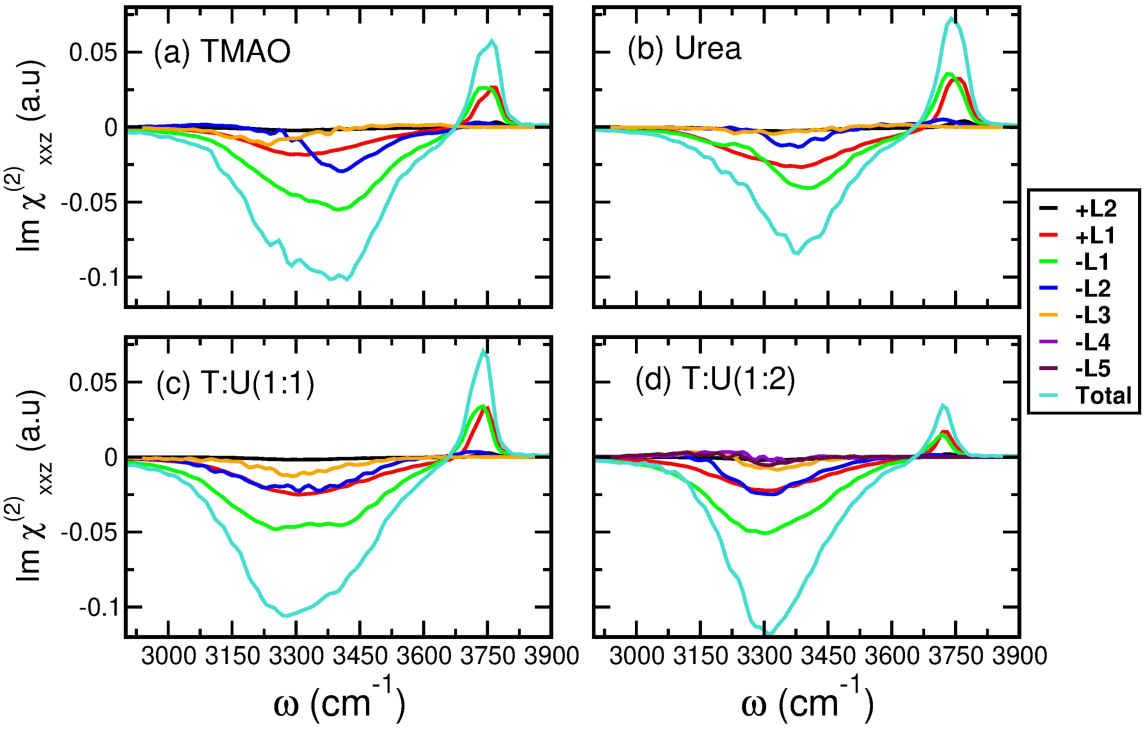

Figure S5: Contributions of different interfacial layers to the total Im $\chi^{(2)}$ spectrum for the binary (a) TMAO, (b) urea, and ternary (c) TMAO: urea (1:1) and (d) TMAO: urea (1:2) aqueous mixtures.

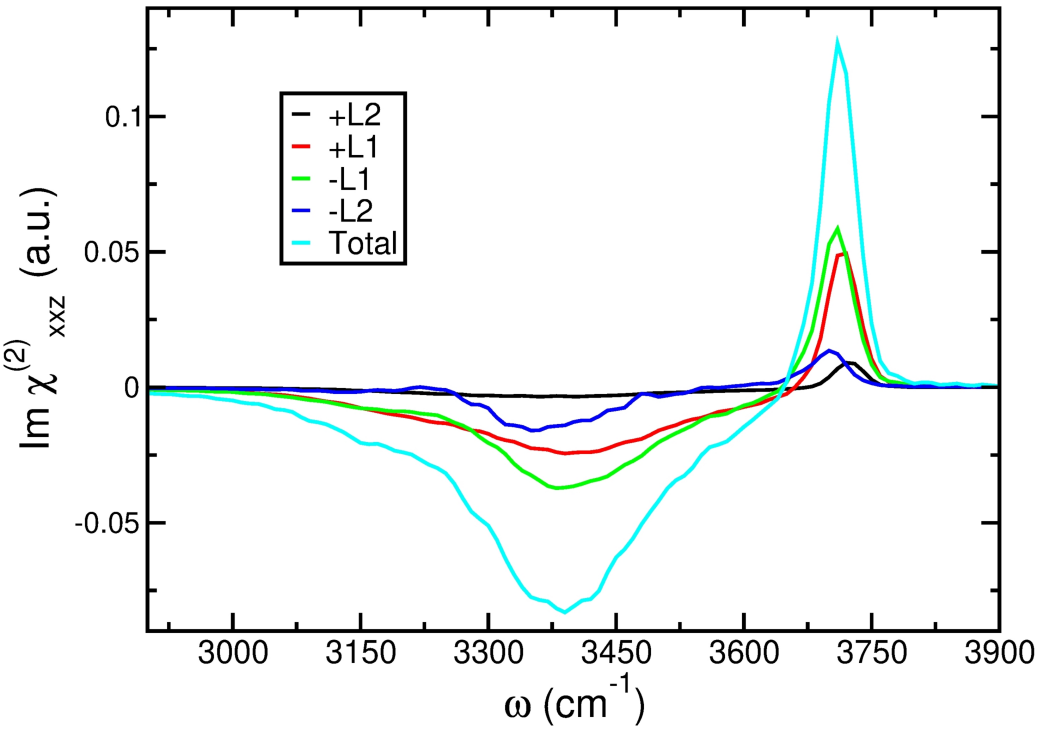

Figure S6: Contributions of different interfacial layers to the total Im $\chi^{(2)}$ spectrum for the neat air-water interface.

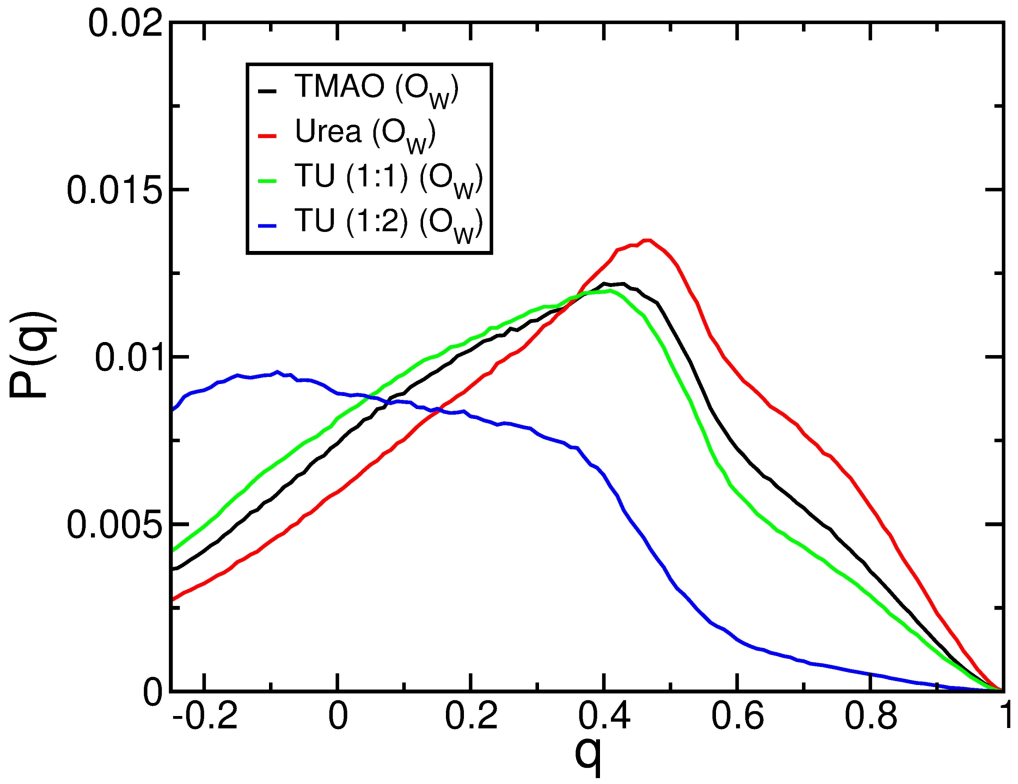

Figure S7: Distributions of the tetrahedral order parameter (q) calculated for interfacial water by considering only the oxygen atoms of water molecules in the binary (a) TMAO, (b) urea, and ternary (c) TMAO: urea (1:1) and (d) TMAO: urea (1:2) aqueous mixtures.