Molecular dynamics (MD) simulation of 2.1M NaI aqueous solution with slab geometry is performed to elucidate the recently reported sum frequency generation (SFG) spectrum from their surface structures. The present MD simulation shows enhanced iodide anions at the surface, which is contrary to the conventional picture of an ion-free surface but is consistent with the recently reported other MD simulations. An electric double layer is formed at the region between the enhanced iodide anions and sodium cations, and thereby the water orientation at the aqueous solution surface is strongly ordered in the opposite direction to the case of pure water. The ssp polarized SFG spectrum calculated for the solution consistently reproduces the experimental spectrum that shows a modest enhancement at the lower frequency region. The modest perturbation of the spectrum in spite of its strongly perturbed water orientation originates from the water-iodide intermolecular correlation effect\(^a\), which has not been considered in the analyses reported so far but is an important effect for such a dielectric media. The electric double layer structure is more strongly reflected in sps spectrum than in ssp spectrum.