THz SFG Spectroscopy of Aqueous Surfaces and Interfaces: Theoretical Studies using Polarizable Force Fields

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Intermolecular interactions and arrangement of water at liquid-vapor interfaces of aqueous solutions are investigated through terahertz (THz) sum frequency generation (SFG) spectroscopic calculations using polarizable models. The main features of intermolecular modes of water in the THz region, namely the libration and hydrogen bond stretch modes, and their anisotropic nature at the interfaces are investigated [1]. The total THz SFG spectrum is dissected into contributions from permanent and induced dipole moments which exhibit oppositely oriented peaks, showing opposite orientations of the permanent and induced dipoles along the hydrogen bonds at the air-water interfaces. The observed broadening of the librational mode of interfacial water is attributed to the heterogeneity of the hydrogen bond network at the interface, as shown by the self and cross correlation contributions for different hydrogen bonding environments at the interfaces. The THz-SFG spectral results of the liquid-vapor interface of water are also compared with those of the mid-IR SFG spectrum of air-water interface and also with the results of linear THz spectrum of bulk liquid water. Subsequently, THz SFG results are presented for liquid-vapor interfaces of aqueous sodium halide solutions [2].

References:

[1] S. Dan, R. Dey, and A. Chandra, J. Phys. Chem. B, **129**, 6069 (2025).

[2] R. Dey, S. Dan and A. Chandra, to be published.