Sum Frequency Generation Orientation Analysis of Molecular Ammonia on the Surface of Concentrated Solutions

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Ammonia-water complexes have been detected with sum frequency generation (SFG) at the liquid/vapor interface of concentrated ammonia solutions ($0.3x$ NH_3, x = bulk mole fraction). SFG spectra taken with the *ssp* polarization combination (*s*-polarized sum frequency signal, *s*-polaried visible light, *p*-polarized infrared beam) are dominated by the N-H symmetric stretch (ν_1) at 3312 cm^{-1} and a weaker deformation mode ($2\nu_4$) at 3200 cm^{-1}. The dangling (free) OH peak due to water at 3700 cm^{-1} is suppressed at this concentration, indicating that water molecules are complexed through hydrogen bonds to ammonia at the interface. The polarization dependence of ν_1 indicates that the NH_3 C_3 molecular axis is tilted with respect to the surface normal by $\theta<38^o$. Variation of the antisymmetric stretch, ν_3, sum frequency signal intensity with polarization restricts the lower limit for surface ammonia tilt angles such that $25^o<\theta<38^o$. Based on this orientation, the structure of the ammonia-water complex is discussed.