

界面における水の核の量子効果

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Nuclear Quantum Effects at the Water-Vapor Interface

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Using combined theoretical and experimental approaches, we demonstrate that the bond orientation of water at the water-vapor interface depends markedly on the water isotope (H/D) composition. While the interfacial water structures of H_2O and D_2O are indistinguishable, the intramolecular symmetry breaking in HDO is directly reflected at the surface: the OD bonds preferably orient down towards the bulk water, whereas the OH bond tends to orient up into the vapor phase. Path integral molecular dynamics simulations show good agreement with surface-specific sum-frequency generation (SFG) spectroscopy results, revealing that the distinct interfacial bond orientations originate from nuclear quantum effects. The enhanced localization of the heavier D atom leads to stronger hydrogen bonds, giving rise to OD bonds of HOD molecules preferentially pointing down into the bulk.

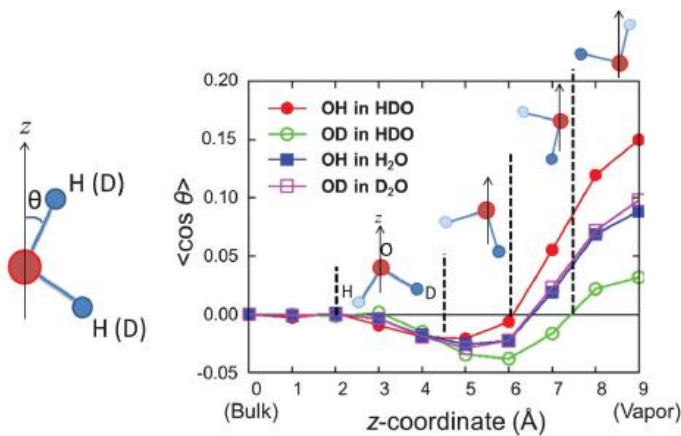


Fig. 1. (Left) Pictorial representation of the angle θ between the OH (OD) bond and the surface normal. (Right) Axial distribution of average angles $\langle \cos \theta \rangle$. Lines are to guide the eye. The water molecules illustrate the average orientations of HDO (D dark blue, H light blue) in the different regions. The positive and negative z axis points up to the vapor region and to the bulk water region, respectively.

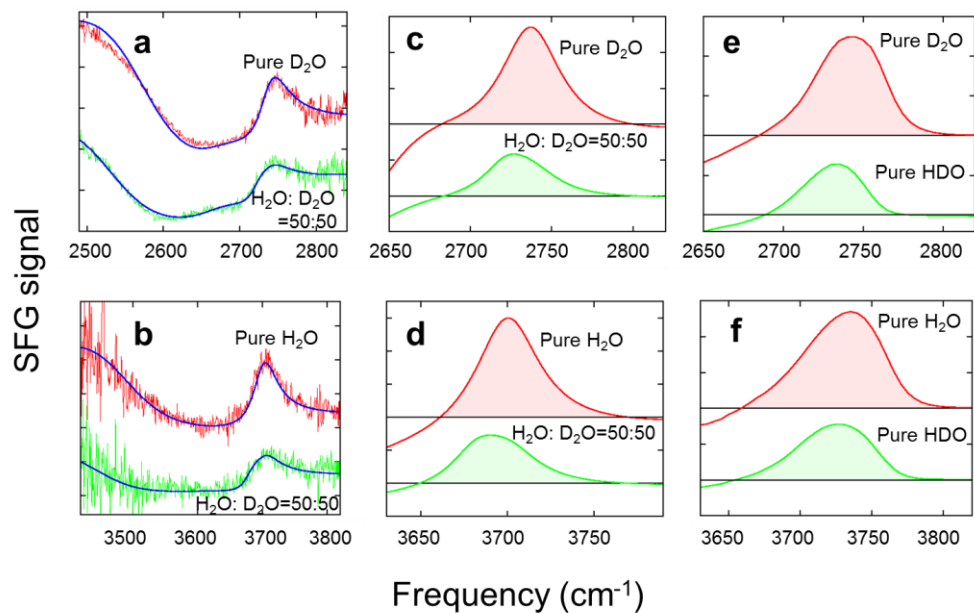


Fig. 2. (a, b) Experimentally measured SFG spectra (red and green) and their fitted curves (blue), (c, d) reconstructed from the fit parameters, and (e, f) simulated. Top panels (a), (c), (e) and down panels (b), (d), (f) display the spectra in the OD and OH stretching regions, respectively. Filled areas in (c), (d), (e), and (f) represent the free OH or OD bond peak areas.

Reference: Y. Nagata, R. E. Pool, E. H. G. Backus, and M. Bonn, *Phys. Rev. Lett.*, **109**, 22610 (2012).