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Nanodroplet Ionization

WALLACE HUI AND KONO LEMKE
University of Hong Kong

Water nanodroplets, formed through rapid cooling and supersaturation of hot aqueous vapors in fumarolic environments, exhibit densities and water network structures distinct from bulk water [1]. These nanodroplets consisting of ~100-1000 H_2O, with unique surface and interior fluid environments, can be regarded as an alternate metal transport media, co-existing with the conventional bulk aqueous and vapor phases.

In this study, we employed *ab initio* molecular dynamics (AIMD) and thermodynamic integration to determine water dissociation ($2H_2O = H_3O^+ + OH^-$) free energies ΔG and ionization constants pK_{aq} in $(H_2O)_{100}$ nanodroplets, focusing on droplet surface and interior ionizations from 25°C to 250°C. At 25°C, BLYP AIMD calculations yield ΔG = 17.6 kcal/mol in the droplet interior region, which corresponds to pK_{aq} = 12.9, aligning with the bulk aqueous values (BLYP pK_w = 15.1, electrical conductivity measured pK_w = 14.0 [2]). In contrast, surface water ionization is less favorable at ΔG = 27.8 kcal/mol (pK_{aq} = 20.4), indicating surface stabilization of water molecules, with a ~10 kcal/mol difference between droplet surface and interior ΔG. At 100°C, surface and interior ΔG values shift to 28.1 kcal/mol (pK_{aq} = 16.5) and 20.5 kcal/mol (pK_{aq} = 12.0), respectively, i.e. the surface-interior energy difference is slightly reduced at ~7 kcal/mol compared to 25°C. At higher temperatures, surface ΔG values are calculated at 28.2 kcal/mol (pK_{aq} = 13.0) at 200°C and 32.4 kcal/mol (pK_{aq} = 13.5) at 250°C. The elevated surface ionization ΔG, in particular at 250°C, reflects enhanced evaporation at the droplet interface, leading to a more disrupted water network, thus inhibiting proton transfer to a neighboring water molecule. Ongoing work extends this approach to higher temperatures (e.g. 350°C), to probe the impact of intensified evaporation and further water network disruption at higher temperatures on nanodroplet ionization properties.

[1] Factorovich, M. H., Molinero, V., & Scherlis, D. A. (2014), *Journal of the American Chemical Society* 136, 4508-4514.

[2] Arcis, H., Ferguson, J. P., Cox, J. S., & Tremaine, P. R. (2020), *Journal of Physical and Chemical Reference Data* 49, 033103.

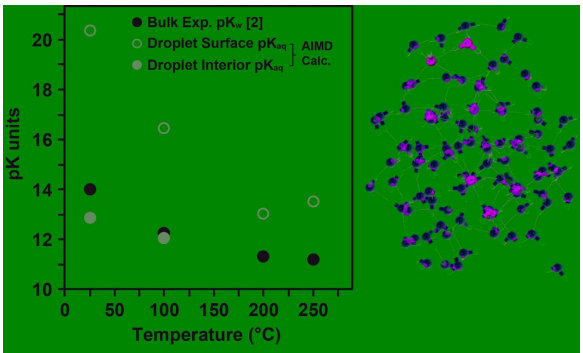

Figure. Comparison of calculated $(H_2O)_{100}$ nanodroplet surface and interior pK_{aq} values against bulk aqueous experimental pK_w [2] (Left). Snapshot of $(H_2O)_{100}$ nanodroplet at 100°C, highlighting a surface $OH^- – H_3O^+$ ion pair at a constrained distance $r_{O\text{-}H}$ = 2.0 Å (Right).