

Investigating the extended hydration of a polyelectrolyte with second-harmonic scattering

J. Dedic¹, H. I. Okur¹, S. Roke^{1*}

¹Laboratory for fundamental BioPhotonics, Institute of Bioengineering, and Institute of Materials Science, School of Engineering, and Lausanne Centre for Ultrafast Science, EPFL

Natural polyelectrolytes form a key part of living tissue while synthetic ones find many industrial applications. However, the behavior of aqueous polyelectrolyte solutions is an ongoing question that relates to the function polyelectrolytes in their respective environments. We investigate the hydration of a naturally occurring polyelectrolyte – hyaluronan (HA), using angle-resolved femtosecond elastic second-harmonic scattering. Our measurements show that the structure of water in a solution of HA is altered in a specific manner compared to the structure of pure water or salt water. Hyaluronan chains are hydrated by a shell of water extending up to hundreds of nanometers. Further investigation of the effect also reveals an increase in water-water orientational correlations in the bulk - the hydrogen bond network of water is becoming stiffer. The effect of HA on the bulk water differs by an order of magnitude between H₂O and D₂O due to a difference in the H-bonding capacities of the two isotopes of water. The sensitivity of second-harmonic scattering to polyelectrolyte hydration offers new insight into the complex behavior of polyelectrolyte solutions. Our observations support the generally accepted idea that polyelectrolytes are well hydrated due to the presence of ionized functional groups. The measurements further show that polyelectrolytes have a longer-range effect on the bulk water than was previously hypothesized.