PhD Thesis Abstract
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This thesis deals with the in-depth understanding of molecular level interactions between ions, water and biologically relevant small molecules using Raman and fluorescence techniques. Raman spectroscopy in combination with multivariate curve resolution (Raman-MCR) has been used extensively to understand the structure and properties of water, such as hydrogen-bonding, intra/intermolecular coupling, and librational freedom in the hydration shell of ions/hydrophobic molecular groups. The role of molecular interactions in protein-drug binding and synthesis of nanoparticles using the protein as a template have also been addressed.

Interactions involving ions, water, and hydrophilic/hydrophobic solutes are intimately related with various chemical and biological processes. The structure and properties of water, such as hydrogen-bonding, intra/intermolecular vibrational coupling, and librational freedom in the hydration shell of a solute are believed to play key roles in those processes. However, the molecular level understanding of such hydration water is limited, because it is technically difficult to selectively record the vibrational spectrum of water in a hydration shell. In this thesis, Raman-MCR spectroscopy has been used to retrieve the hydration water spectrum (Solute correlated spectrum, SC-Spectrum). The SC-Spectrum reveals the native (label free) characteristics of water at the immediate vicinity of the ions/ hydrophobic solutes. The results have revealed different vibrational response of water in the hydration shell of ions and hydrophobic molecules in the OH stretch, HOH bend, and [bend+librational] combination band regions. Analyses of these hydration water spectra have showed that water is vibrationally decoupled in the hydration shell of ions and hydrophobic molecules. Moreover, H-bond strength of water in the hydration shell of multivalent anions (SO_4^{2-}, CO_3^{2-} and PO_4^{3-}) is stronger than that of bulk water. While, the same is weaker for the monovalent anions (I^-, Br^- and NO_3^-). The librational mobility of hydration water increases as CO_3^{2-} \approx SO_4^{2-} < bulk water < Cl^- < I^- . It is also observed that water forms stronger H-bond in the hydration shell of charged as well as neutral hydrophobic molecular groups. Furthermore, the results show the existence of dangling OH bonds at the surface of hydrophobic molecules, which is coupled with the H-bonded OH stretch vibration of the same water molecule (Intramolecular coupling). This thesis also describes the molecular level interactions between bovine serum albumin (BSA) and hematoporphyrin (HP), a well known photosensitizer used in photodynamic therapy, using steady state as well as time-resolved fluorescence spectroscopy. It has been demonstrated that HP binds with two well-separated sites located in the sub-domain IB and IIA of BSA. Furthermore, it has been demonstrated that the morphology and optical properties of CdSe nanoparticles can be tuned by changing the experimental condition such as varying molar ratio of the precursors, which alter the type of interaction between protein functional groups and surface atoms of QDs. This demonstrates the role of protein-inorganic ion interactions on controlling the shape of CdSe nanoparticles.