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<td>Left: The water molecule. The red sphere represents the oxygen atom and the grey spheres are the hydrogen atoms. The $\delta^+$ and $\delta^-$ signs indicate the relative charge. Right: The tetrahedral arrangement of the hydrogen-bonded water network. Hydrogen bonds are indicated with the dashed lines.</td>
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<td>Raman spectrum of water. The water molecules depict the intra (OH stretch (3000 – 3700 cm$^{-1}$) and HOH bend (1600 – 1700 cm$^{-1}$)) and intermolecular (librational band below 1000 cm$^{-1}$) and combination ([bend + librational] band 1950 - 2200 cm$^{-1}$) vibrational modes of water.</td>
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Figure 2.1.

Energy level diagram showing the states involved in the Rayleigh and Raman scattering. Green lines signify incident light, the red line signifies Stokes Raman scattering, and the blue line signify anti-Stokes Raman Scattering. The energy of the incident laser beam is denoted by $hv_0$ and $\Delta E$ represent the vibrational energy of the molecule ($hv_m$).

Figure 2.2.

Polarization (P) induced in a molecule’s electron cloud by an incident optical electric field $\vec{E}$. Scattering may be in various directions.

Figure 2.3.

Diatomuc Molecule as a Spring-Mass System

Figure 2.4.

Optical layout of the of Micro-Raman Instrumentation

Figure 2.5.

Schematic diagram of TCSPC setup

Figure 3.1.

Concentration normalized Raman spectra of (A) $D_2O$ in the OD stretch regions (B) $H_2O$ in the OH stretch regions with different mole fractions of NaBr as mentioned in the panel.

Figure 3.2.

Concentration normalized Raman spectra of $D_2O-H_2O$ mixtures in the OD
stretch regions with different mole ratios as mentioned in the panel.

**Figure 3.3.**

Plot of integrated Raman intensity (OD stretch band) against the mole fraction of NaBr in D$_2$O (red) or the volume fraction of H$_2$O in D$_2$O (blue).

**Figure 3.4.**

Raman spectra of isotopically diluted water (A) (D$_2$O/HOD/H$_2$O = 1/18/81) in the OD stretching regions (B) (D$_2$O/HOD/H$_2$O = 81/18/1) in the OH stretching regions with different mole fractions of NaBr. The spectra were normalized according to Eq.3.2.

**Figure 3.5.**

(A) Change in FWHM of the OD stretch band with increasing concentration of NaBr in D$_2$O (red circle) and in isotopically diluted water (D$_2$O/HOD/H$_2$O = 1/18/81) (green square) (B) Change in FWHM of the OH stretch band with increasing concentration of NaBr in H$_2$O (red circle) and in isotopically diluted water (D$_2$O/HOD/H$_2$O = 81/18/1) (green square). The dashed lines are guides for the eye.

**Figure 3.6.**

Plot of relative integrated intensity vs. the concentration of NaBr in (A) D$_2$O (black circles) and isotopically diluted water (D$_2$O/HOD/H$_2$O = 1/18/81) (red circles) (B) H$_2$O (black circles) and isotopically diluted water (D$_2$O/HOD/H$_2$O = 81/18/1) (red circles). The solid lines are the fitted functions as mentioned in the text.
Figure 3.7.
Plot of the relative integrated intensity vs. the concentration of MX: NaI (blue), NaBr (green), NaCl (red), and KF (black) in the isotopically diluted water, D₂O/HOD/H₂O = 1/18/81. The solid lines are the fitted functions according to equation 3.6.

Figure 3.8.
Plot of relative Raman cross-section vs. the energy of electronic absorption of water (red circle) for different alkali halide solutions. Blue and green lines are the simulated curves corresponding to the lowest energy (60240 cm⁻¹, top horizontal axis) and higher energy (120000 cm⁻¹, bottom horizontal axis) electronic excited states of water.

Figure 4.1.
Area normalized Raman spectrum of water with different concentration of (A) NaBr (B) NaI (C) NaNO₃ (D) Na₂SO₄ (E) Na₂CO₃, and (F) Na₃PO₄.

Figure 4.2.
Salt-correlated Raman spectra of water in the OH stretch regions for various Na-salts of chaotropic (A) and kosmotropic (B) anions as mentioned in the graph panel. Raman spectra of H₂O (black), HOD (red; H₂O/D₂O = 1/19; v/v), NaNO₃ (green), NaBr (blue), NaI (magenta), Na₃PO₄ (orange), Na₂SO₄ (olive), and Na₂CO₃(violet).
Figure 4.3.

Polarized Raman spectra of water (isotropic (violet), anisotropic (olive) and unpolarized (black dashed line)). Raman spectra of HOD (red dotted line; \( \text{H}_2\text{O}/\text{D}_2\text{O} = 1/19; \text{v/v} \)) is shown for comparison.

Figure 4.4.

Multiple Gaussian peak fits of the Raman spectra of \( \text{H}_2\text{O}, \text{HOD} \) (\( \text{H}_2\text{O}/\text{D}_2\text{O} = 1/19; \text{v/v} \)), and the anion-correlated spectra of Na-salt solutions. The fitted spectra and the corresponding component bands are shown by dashed and dotted lines, respectively.

Figure 4.5.

Variation of (A) Integrated area (B) spectral width (fwhm) of the component bands in the OH stretch regions.

Figure 4.6.

Variation of percentage coupling (intermolecular vibrational coupling and FR) of water in the hydration shells of kosmotropic and chaotropic anions. The coupling in \( \text{H}_2\text{O} \) (undiluted) is assumed as 100 %.

Figure 4.7.

Peak area-averaged wave number \( (\nu_a) \) of anion-correlated spectra in the OH stretch regions.

Figure 4.8.

IC-Raman spectra of \( \text{H}_2\text{O} \) in presence of (A) NaCl (gray), NaI (red), (B)
Na$_2$SO$_4$ (orange), and Na$_2$CO$_3$ (purple). The Raman spectrum of bulk H$_2$O (black line) and MCR-retrieved spectrum of H$_2$O in D$_2$O (green line) that bears the Raman response of decoupled H$_2$O (around 1650 cm$^{-1}$) are shown in both panels.

**Figure 4.9.**

Variation of (A) peak position and (B) width (fwhm) of the HOH bend mode of water with the concentration of Na-salts (salts are mentioned in the graph panel).

**Figure 4.10.**

Background subtracted Raman spectrum (red) of H$_2$O in hindered rotational band regions (400 – 1000 cm$^{-1}$). Gray line is the fitted spectrum, olive and blue lines are the Gaussian component bands.

**Figure 4.11.**

Peak normalized IC-Raman spectra for (A) NaI and NaCl (B) Na$_2$SO$_4$ and Na$_2$CO$_3$ in the combination ($v_B$ + $v_{L_1}$) band regions. The Raman spectrum of neat H$_2$O (black) is shown in each panel for comparison with the IC-spectra.

**Figure 5.1.**

Raman spectra of neat water (black line), TBA (1.0 mole dm$^{-3}$) in H$_2$O (blue line) and in D$_2$O (red dashed line) in 2900 – 3750 cm$^{-1}$ region.

**Figure 5.2.**

TBA-correlated Raman spectrum of water (red) in 2900 – 3750 cm$^{-1}$ region. Raman spectrum of neat water (black) is shown for reference. **Inset:**
expanded view of the TBA-correlated spectrum in the high frequency region that shows the dangling OH at the surface of TBA.

**Figure 5.3.**

TBA-correlated spectrum (red dashed curve) and polarized Raman spectra of bulk water (isotropic (blue), anisotropic (green) and unpolarized (black)) in 3000 - 3800 cm\(^{-1}\) region.

**Figure 5.4.**

(A) Global fitting of the normalized Raman spectra of neat H\(_2\)O and isotopically diluted water (HOD75 [H\(_2\)O/D\(_2\)O = 75/25]; HOD50 [H\(_2\)O/D\(_2\)O = 50/50], and HOD25 [H\(_2\)O/D\(_2\)O = 25/75]) with three component Gaussian fitting functions. Dotted lines represent the fitting functions. (B) Plot of amplitude of the component bands (dashed lines: black (3208 cm\(^{-1}\)), red (3422 cm\(^{-1}\)), and green (3613 cm\(^{-1}\))) vs. the mole fraction of O-H oscillators in water. Variations of relative integrated intensity above 3400 cm\(^{-1}\) (red solid line) and below 3400 cm\(^{-1}\) (black solid line) vs. the mole fraction of O-H oscillators are shown in the same panel.

**Figure 5.5.**

SC-Raman spectra of water (red solid line) in the OH stretch regions for H\(_2\)O and H\(_2\)O-D\(_2\)O mixtures as mentioned in the graph panels. Experimentally recorded Raman spectra (green dashed line) of 1.0 mol dm\(^{-3}\) aqueous solutions of NaCl (left panel, A1-A4), TBA (middle panel, B1-B4), and TMACl (right panel, C1-C4) and that of bulk water (black solid line) are
shown in respective panels for references. The dashed black line in the right panel is the experimental Raman spectra of 1.0 mol dm$^{-3}$ aqueous NaCl solution.

**Figure 5.6.**

Plot of Relative integrated intensity (RI) of the SC-spectra against the mole fraction of OH oscillator ($X_{OH}$) in bulk H$_2$O-D$_2$O mixtures. RI$>3400$ and RI$<3400$ are the relative integrated intensity of the OH stretch band above and below 3400 cm$^{-1}$. Dotted and dashed-dotted lines are visual guide to the variations of RI$<3400$ and RI$>3400$ respectively.

**Figure 5.7.**

**Left panel:** Variation of dangling OH band with isotopic dilution in the hydration shell of TBA. **Right panel:** Dangling OH band of HOD (orange dashed line; orange solid line is the Lorentz fitting function) and H$_2$O (black dashed line; black solid line is the Lorentz fit function) in the hydration shell of TBA. The dangling OH band of HOD is obtained by a second MCR analysis of the TBA-correlated spectra in H$_2$O (100%) and H$_2$O (25%).

**Scheme 5.1.**

Model diagram showing the intramolecular vibrational coupling and the dangling OH band positions of H$_2$O and HOD in hydrophobic hydration shell. In H$_2$O, the dangling OH (H$_2$O) is shifted to higher frequency (blue-shift) from that of decoupled dangling OH, due to strong intramolecular coupling with H-bonded OH stretch ($\sim 3430$ cm$^{-1}$). In HOD, because of the
large energy gap between the dangling OH (HOD) and the H-bonded OD stretch (~2510 cm\(^{-1}\)), the intramolecular coupling is weak, and the dangling OH (HOD) band is close to that of decoupled dangling OH.

**Figure 6.1.**

(A) Chemical structure of the molecules with methyl groups attached with different neighboring atoms/groups of varying charge. The counter ion (Cl\(^-\)) in TMA is omitted for simplicity. (B) Motivation (schematic): Interaction of a methyl group and water can be probed by measuring the CH\(_3\) stretch vibration (Raman band). X is the atom/group attached with the methyl group.

**Figure 6.2.**

Vibrational (Raman) spectra of (A) TBA (0.01 mole fraction) and (B) TMAO (0.01 mole fraction in water but less in CDCl\(_3\)) in the CH stretch regions, in CDCl\(_3\) (black) and neat water (red). Dotted line in the panel A is the Raman spectrum of TBA in CCl\(_4\). The spectra are normalized at the high frequency CH stretch band. The low S/N in the black spectrum in the bottom panel is due to poor solubility of TMAO in CDCl\(_3\). The spectrum of TMAO in CCl\(_4\) could not be recorded because of insolubility of TMAO.

**Figure 6.3.**

Vibrational (Raman) spectra of TBA in the CH stretch regions (A) with varying concentration of TBA in water and (B) in different aqueous potassium halide solutions (0.01 mole fraction of TBA). Concentrations of potassium halides and TBA are mentioned in the graph panels. The spectra
are normalized at the high frequency CH stretch band.

**Figure 6.4.**

Vibrational (Raman) spectra of TMAO (0.01 mole fraction) in the CH stretch regions, (A) in different aqueous media and (B) in aqueous solution with different concentrations of KI. The spectra are normalized at the high frequency CH stretch band.

**Figure 6.5.**

Vibrational (Raman) spectra of TMA⁺ (conc. = 0.01 mole fraction) in the CH₃ stretch regions, in different aqueous media. Concentrations of potassium halides are mentioned in the graph panels. The spectra are normalized at the CH₃(AS) stretch band.

**Figure 6.6.**

Plot of relative position of Raman bands ($ν/ν₀$; $ν$ is the vibrational band position in different solvents and $ν₀$ is the band position in apolar CDCl₃) vs. $E_T^N$ values for the C=O stretch of acetone (black circle) and CH₃(AS) of acetone (green circle), TBA (red circle), and TMAO (blue circle). The dashed lines are guide to eye for the variation of $ν/ν₀$.

**Figure 7.1.**

Chemical structure of Hematoporphyrin (HP)

**Figure 7.2.**

Steady-state absorption (solid line) and fluorescence (dotted line) spectra of BSA (black) and HP (red) in Tris-HCl buffer (pH = 7.4).
Figure 7.3.
(A) Fluorescence spectra of BSA (1.0 µM) in the absence and presence of HP in Tris-HCl buffer solution. Concentration of HP in µM: (i) 0, (ii) 0.25, (iii) 0.5, (iv) 1.0, (v) 2.0, (vi) 3.0, (vii) 4.0, and (viii) 5.0, respectively. (B) Plot of $F_0/(F_0-F)$ against $1/[HP]$ at three different temperatures as per the modified Stern-volmer equation.

Figure 7.4.
(A) Fluorescence decay profiles ($\lambda_{ex}$=292 nm, $\lambda_{em}$=340 nm) of BSA in the absence (a) and presence of (b) 1µM and (c) 5µM HP. The scattered points represent actual decay profile while the solid dark yellow line represents a tri-exponential fit to that decay. (B) Plot of $\tau_0/\tau$ vs. the concentration of HP.

Figure 7.5.
(Fluorescence spectra of BSA as a function of HP concentrations. Inset shows background subtracted fluorescence spectra of HP obtained by the 280 nm photo excitation of BSA (1µM). Concentrations of HP in µM (i) 0.25 (ii) 0.5 (iii) 1.0 (iv) 3.0 and (v) 5.0.

Figure 7.6.
(A) UV-visible absorption spectra of BSA in the presence of HP. (a) the absorption spectra of BSA-HP system; (b) the absorption spectra of BSA only; (c) the difference absorption spectra between BSA-HP and HP; (d) the absorption spectra of HP only. [BSA]=1µM and [HP] =3µM (B) van’t Hoff
plot for the interaction of BSA with HP in Tris-HCl buffer (pH=7.4).

**Figure 7.7.**

Overview of the binding sites of HP in (A) subdomain IB and (B) IIA of BSA.

**Figure 7.8.**

Stereo view of HP inside subdomain (i) IB and (ii) IIA of BSA obtained by using refined grid covering. The amino acid residues (in different colors) forming the binding cavity and H-bonds (as highlighted by the dashed lines in red color) formed between HP with BSA.

**Figure 7.9.**

(A) Plot of RMSD of C-Cα-N backbone against simulation time scale (ps) for solvated BSA and BSA-HP during 10 ns MD Simulation. (B) Plot of Rg during 10 ns MD simulation of BSA and BSA-HP complex.

**Figure 7.10.**

HP bound to subdomain IB binding site after 10 ns of simulation. The H-bonds are depicted with red dash lines.

**Figure 7.11.**

Plot of RMSF values of BSA, its complex with HP and the difference (complex-BSA) against residue number.

**Figure 8.1.**

XRD pattern for BSA-CdSe QDs synthesized with molar ratio ([Cd$^{2+}$]: [Se$^{2-}$], in mM) of 20:10. [BSA] = 1 mg/ml.
**Figure 8.2.**

TEM images of BSA-CdSe nanoparticles synthesized with molar ratio ([Cd$^{2+}$]: [Se$^{2-}$], in mM) of: (a) 20:10 (Inset: SAED pattern), (b) 20:10, (c) 10:10, (d) 10:20. [BSA] = 1 mg/ml.

**Figure 8.3.**

Raman Spectra of BSA-CdSe nanoparticles synthesized with molar ratio ([Cd$^{2+}$]: [Se$^{2-}$], in mM) of 20:10. [BSA] = 1 mg/ml.

**Figure 8.4.**

SEM images of BSA-CdSe nanoparticles synthesized with molar ratio ([Cd$^{2+}$]: [Se$^{2-}$], in mM) of: (a) & (b) 20:10, (c) 10:10, (d) 10:20. [BSA] = 1 mg/ml. Inset of image (a) shows the % distribution plot of the oval and hexagonal shapes of CdSe.

**Figure 8.5.**

SEM images showing the presence of the 1-D (nanorods) structures of CdSe with molar ratio ([Cd$^{2+}$]: [Se$^{2-}$], in mM) of 20:10. [BSA] = 1 mg/ml.

**Figure 8.6.**

SEM images showing the presence of the spherical globular like nanostructures of CdSe with molar ratio ([Cd$^{2+}$]: [Se$^{2-}$], in mM) of 10:10. [BSA] = 1 mg/ml.

**Scheme 8.1.**

Diagrammatic representation of the formation of different morphologies of
BSA-CdSe nanoparticles synthesized with their respective molar ratio of the precursors. [BSA] = 1 mg/ml.

**Figure 8.7.**

Camera ready pictures of the BSA-CdSe nanoparticles synthesized with molar ratio ([Cd²⁺]: [Se²⁻], in mM) of: (a) 10:5 (light green), (b) 10:10 (yellowish orange), (c) 10:20 (orange), (d) 10:40 (bright red). [BSA] = 1 mg/ml.

**Figure 8.8.**

(A) Optical absorption spectra of BSA-CdSe QDs synthesized with molar ratio ([Cd²⁺]: [Se²⁻], in mM) of: (a) 10:5; (b) 10:10; (c) 10:20; (d) 10:40. (B) Tauc plot of (αhv)² vs. hv for the determination of energy band gap, E_g. [BSA] = 1 mg/ml.

**Figure 8.9.**

Normalized room temperature PL spectra of BSA-CdSe QDs synthesized with molar ratio ([Cd²⁺]: [Se²⁻], in mM) of: (a) 10:5; (b) 10:10; (c) 10:20; (d) 10:40. (B) Corresponding room temperature PL spectra of BSA-CdSe QDs with their respective molar ratios (in mM). [BSA] = 1 mg/ml.

**Figure 8.10.**

Room temperature time resolved PL decay curve (λ_exc. = 450 nm) of BSA-CdSe QDs with molar ratio ([Cd²⁺]: [Se²⁻], in mM) of: (a) 10:20 (b) 10:40. [BSA] = 1 mg/ml.
Figure 8.11.

(A) Optical absorption spectra of BSA-CdSe QDs synthesized with molar ratio ([Cd$^{2+}$]: [Se$^{2-}$], in mM) of: (a) 2.5:10; (b) 5:10; (c) 10:10; (d) 20:10. (B) Tauc plot of $(\alpha'\hbar\nu)^2$ vs. $\hbar\nu$ for the determination of energy band gap, $E_g$. [BSA] = 1 mg/ml.

Figure 8.12.

Normalized room temperature PL spectra of BSA-CdSe QDs synthesized with molar ratio ([Cd$^{2+}$]: [Se$^{2-}$], in mM) of: (a) 2.5:10; (b) 5:10; (c) 10:10; (d) 20:10. Inset: Corresponding room temperature PL spectra of BSA-CdSe QDs with their respective molar ratios (in mM). [BSA] = 1 mg/ml.

Figure 8.13.

Plots showing the trend in the variation of $\lambda_{max}$ (PL) and PL intensity at different molar ratio of precursors, keeping concentration of Cd$^{2+}$ (A) and Se$^{2-}$ (B) constant, respectively.

Figure 8.14.

Energy level diagram showing the band gap levels and the trap state levels in four different CdSe QDs formed in four different conditions with [Cd]:[Se] ratios (in mM) of 10:5, 10:10, 10:20 and 10:40.

Figure 8.15.

Optical absorption spectra of (a) BSA, (b) BSA-Cd$^{2+}$ and (c) BSA-CdSe. Inset: Camera-ready pictures of (a) BSA, (b) BSA-Cd$^{2+}$ and (c) BSA-CdSe.
solutions.

Figure 8.16. 200

FT-IR spectra of (a) pure BSA and (b) BSA-CdSe QDs.

Scheme 8.2. 201

Proposed mechanism of formation of CdSe QDs in the host matrix of BSA