

Electronic Supplementary Information for
Vibrational Probing of the H-bond Structure and Dynamics of
Water in Aqueous NaPF₆ Solutions

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1. Decomposition of the OD stretch band into three contributions (OD_w, OD_C, and OD_A)

$$\begin{aligned}
 S(\omega) &= \alpha \cdot S_{\text{OD}_w}(\omega) + S_{\text{OD}_C}(\omega) + S_{\text{OD}_A}(\omega) \\
 &= \alpha \cdot S_{\text{OD}_w}(\omega) \\
 &+ A_1 \left\{ m_1 \frac{2}{\pi} \frac{w_1}{4(\omega - \omega_1)^2 - w_1^2} + (1 - m_1) \sqrt{\frac{4 \log 2}{\pi}} \frac{1}{w_1} \exp \left[-4 \log 2 \frac{(\omega - \omega_1)^2}{w_1^2} \right] \right\} \\
 &+ A_2 \left\{ m_2 \frac{2}{\pi} \frac{w_2}{4(\omega - \omega_2)^2 - w_2^2} + (1 - m_2) \sqrt{\frac{4 \log 2}{\pi}} \frac{1}{w_2} \exp \left[-4 \log 2 \frac{(\omega - \omega_2)^2}{w_2^2} \right] \right\}
 \end{aligned}$$

where α is the scaling factor for the OD stretch band of neat water (OD_w). The second and third terms are the pseudo Voigt profiles to fit the OD_C and OD_A peaks, respectively. The results of decomposition of FTIR spectra into three contributions are shown in Figures S1.

2. Raman experimental setup

Our Raman experimental setup consists of a 100 mW 532 nm laser and a monochromator coupled with a CCD camera. A Raman edge filter was placed in front of the monochromator to attenuate the intense Rayleigh scattering. The average spectral resolution is $\sim 1.7 \text{ cm}^{-1}$.

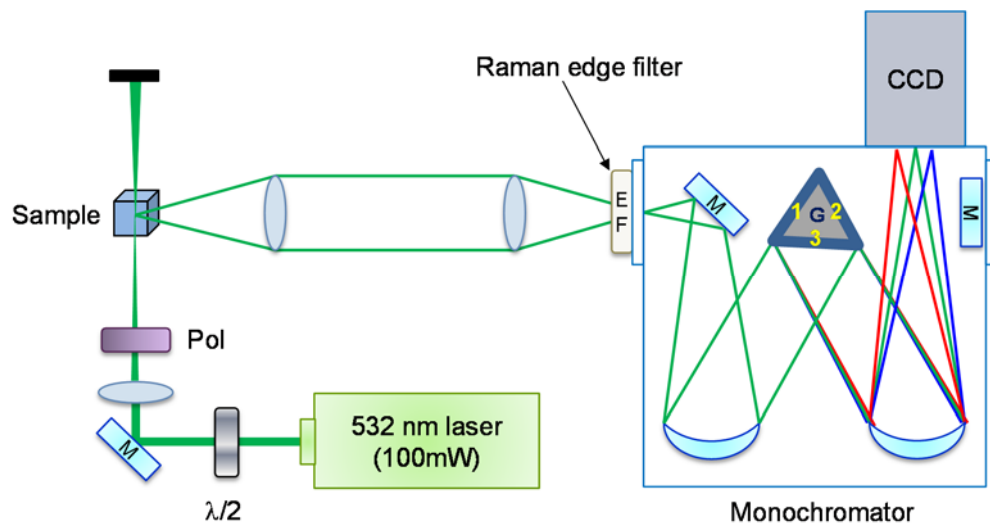


Table S1. Fit parameters of the decomposition of FTIR spectra into three contributions

	ω_1 (cm ⁻¹)	A ₁	w_1 (cm ⁻¹)	m_1	ω_2 (cm ⁻¹)	A ₂	w_2 (cm ⁻¹)	m_2	α
1.0 M	2541±1	13.2±0.1	150±1	0.08±0.01	2669±1	2.07±0.1	30±1	0.60±0.01	0.68±0.01
3.0 M	2541±1	24.8±0.1	150±1	0.08±0.01	2669±1	5.1±0.1	30±1	0.60±0.01	0.39±0.01
5.0 M	2541±1	31.1±0.1	150±1	0.08±0.01	2669±1	8.2±0.1	30±1	0.60±0.01	0.18±0.01

Table S2. Fit parameters of the decomposition of Raman spectra into three contributions

	ω_1 (cm ⁻¹)	A ₁	w_1 (cm ⁻¹)	m_1	ω_2 (cm ⁻¹)	A ₂	w_2 (cm ⁻¹)	m_2	α
1.0 M	2556±1	47±1	143±1	0	2665±1	31±1	39±1	0.78±0.01	0.75±0.01
3.0 M	2556±1	113±1	143±1	0	2665±1	73±1	34±1	0.74±0.01	0.44±0.01
5.0 M	2556±1	125±1	143±1	0	2665±1	103±1	32±1	0.75±0.01	0.25±0.01

Figure S1.

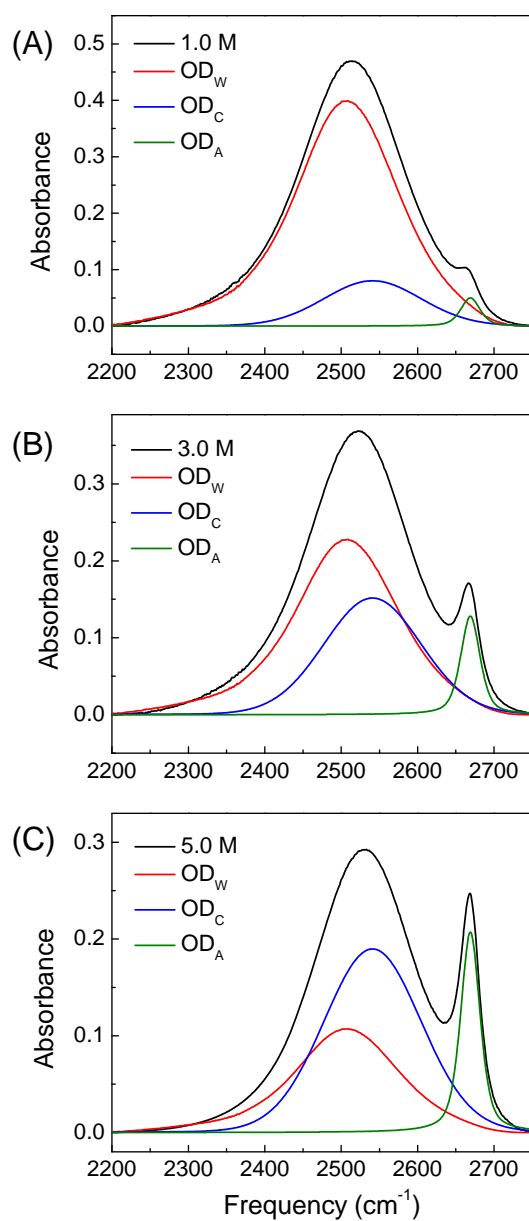


Figure S1. Decomposition of the OD stretch band in the FTIR spectra into three contributions (OD_W , OD_C , and OD_A) in 1.0, 3.0, and 5.0 M NaPF_6 solutions.

Figure S2

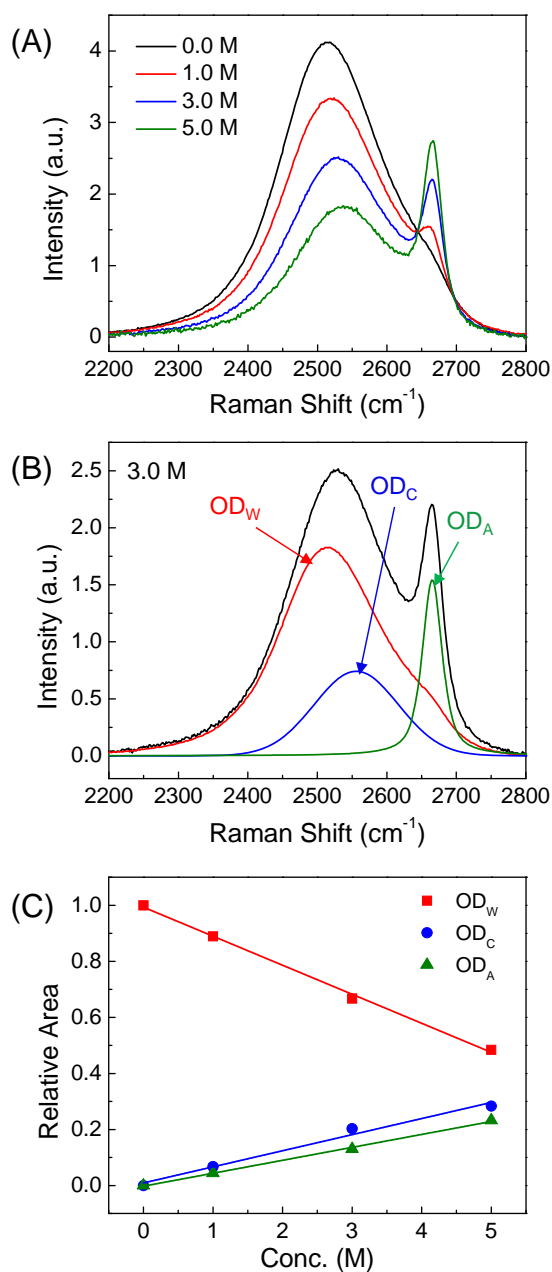


Figure S2. (A) The OD stretch band in the Raman spectra measured with aqueous NaPF₆ solutions at different concentrations. (B) Decomposition of the OD stretch band into three contributions: the OD stretch band of water in bulk (OD_w), hydration shells of Na⁺ ions (OD_c), and hydration shells of PF₆⁻ ions (OD_a). (C) Relative areas of three OD stretch peaks are plotted as a function of concentration.

Figure S3.

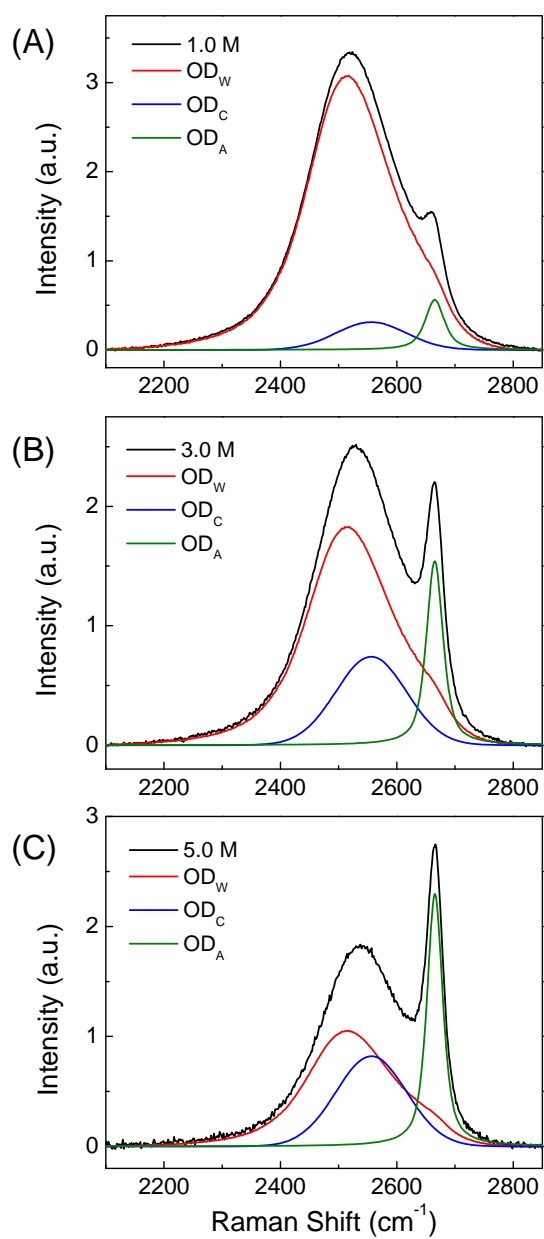


Figure S3. Decomposition of the OD stretch band in the Raman spectrum into three contributions (OD_W, OD_C, and OD_A) in 1.0, 3.0, and 5.0 M NaPF₆ solutions.

Figure S4

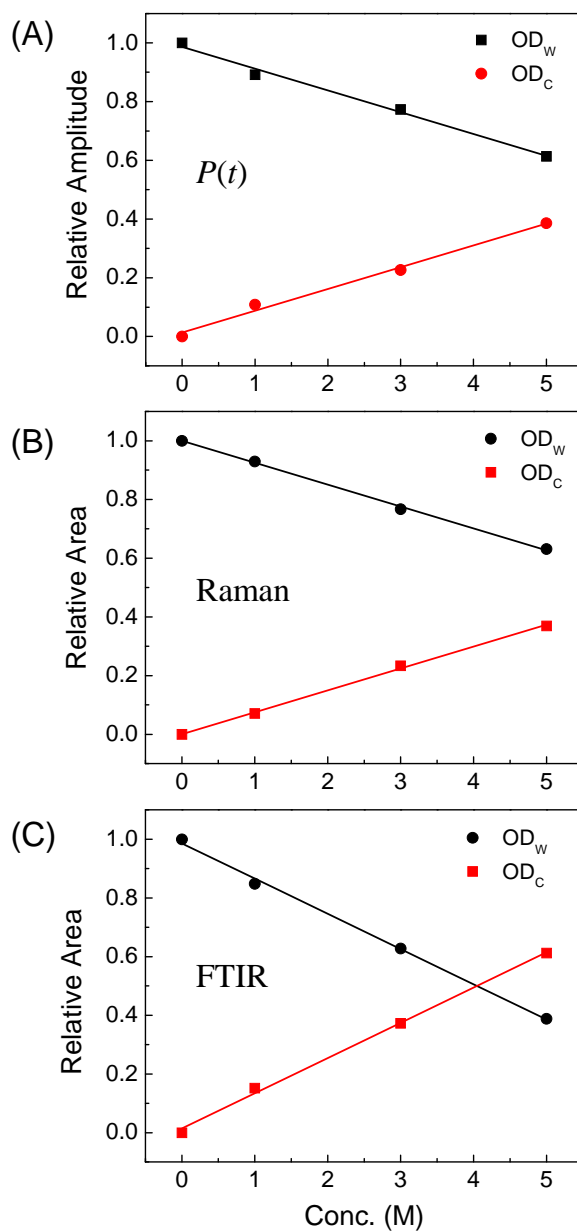


Figure S4. Results of two-state model analysis. (A) Relative amplitudes of two components (OD_w and OD_c) in population decay, $P(t)$. (B) Relative areas of two subsets (OD_w and OD_c) in Raman spectrum. (C) Relative areas of two subsets (OD_w and OD_c) in FTIR spectrum.