Supporting Information for

TMAO Perturbs

Intermolecular Vibrational Motions of Water

Revealed by the Low-frequency Modes

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1. Polarized HR spectra of water and TBA aqueous solutions.
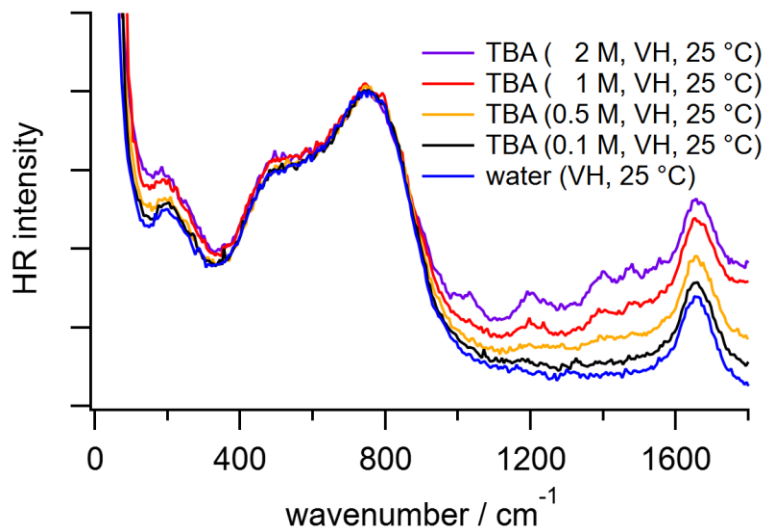

Figure S1. Polarized HR spectra of water (blue) and TBA aqueous solutions at 0.1 M (black), 0.5 M (orange), 1 M (red), and 2 M (purple) measured at 25 ˚C. The polarization directions are vertical (V) for the incident light and horizontal (H) for the scattered light at 90˚, respectively, referred as VH.

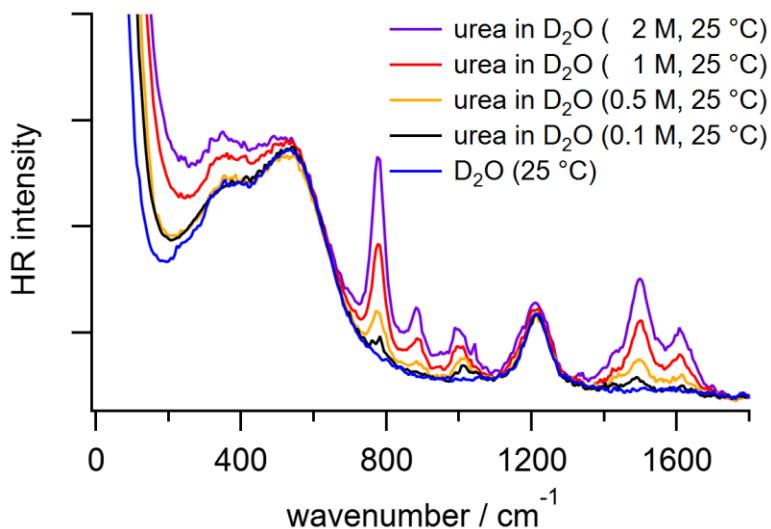**2. HR spectra of heavy water and urea aqueous solutions in D₂O.**

Figure S2. HR spectra of heavy water (blue) and urea aqueous solutions in D₂O at 0.1 M (black), 0.5 M (orange), 1 M (red), and 2 M (purple) measured at 25 ˚C.

All librational and vibrational bands of water downshift due to the isotope effect compared with those in H_2O. In the HR spectrum of D_2O, the DOD bending band and the librational bands are located around 1210, 550 and 360 cm^{-1}, respectively.[S1] The intense intramolecular vibrational band ascribed to the CO wagging mode around 780 cm^{-1} becomes distinguishable even at 0.1 M. A band assigned to a coupling between the CN symmetric stretching and the ND_2 rocking modes newly appears around 890 cm^{-1}.[S2]

3. HR spectra of TMAO, TBA, and urea aqueous solutions at 0.5 M, and water measured at different temperatures.
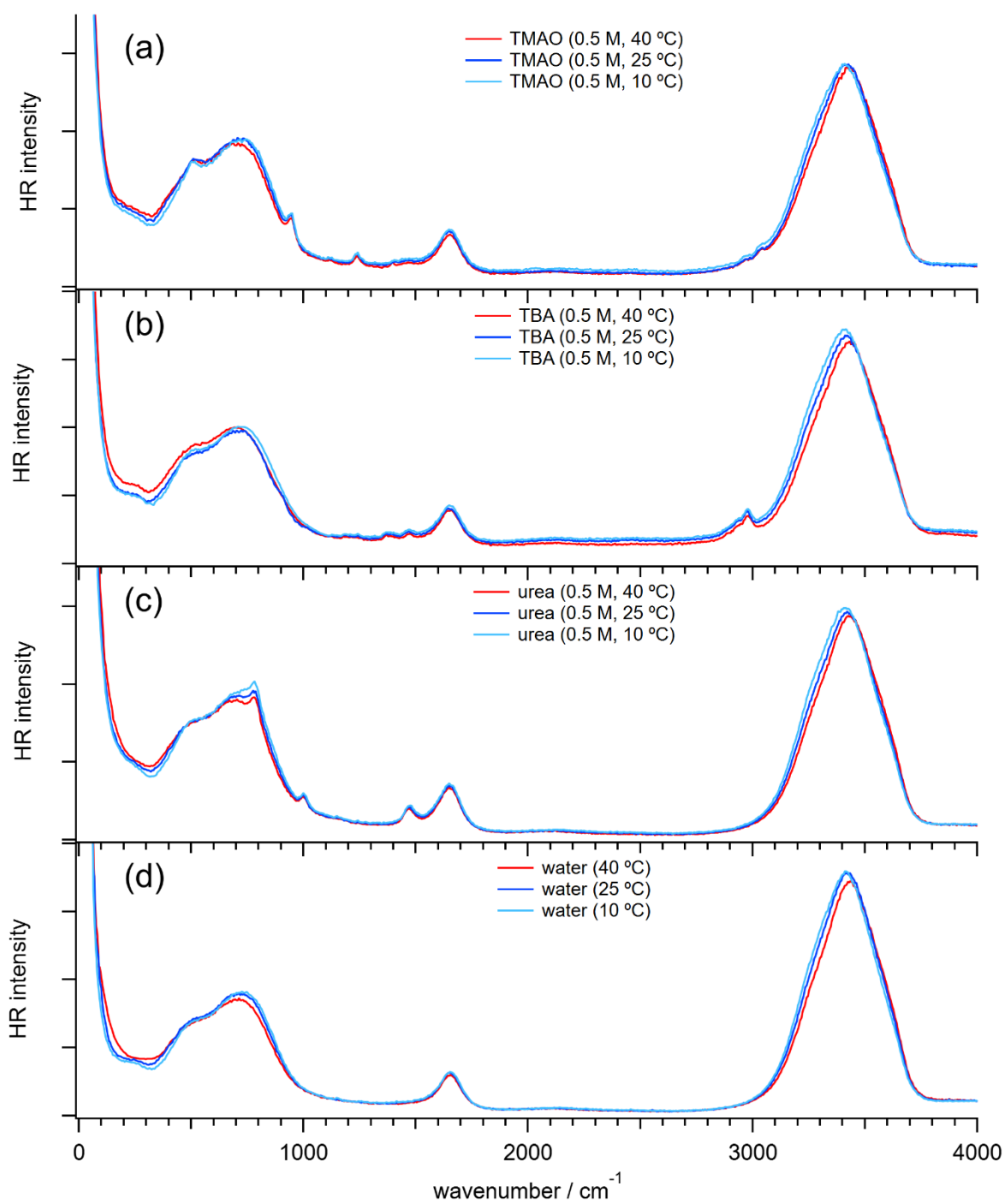

Figure S3. HR spectra of TMAO (a), TBA (b), and urea (c) aqueous solutions at 0.5 M, and water (d) measured at 10 ˚C (light blue), 25 ˚C (dark blue), and 40 ˚C (red).

4. Summary of vibrational modes and frequencies of water in TBA and urea solutions.

Table S1 Vibrational modes and frequencies of water in TBA solutions.

concentration / M	HB / cm^{-1}	L1 / cm^{-1}	L2 / cm^{-1}	HOH bend / cm^{-1}	OH stretch / cm^{-1}
0		479	718	1650	3419
0.1	254	476	722	1650	3419
0.5	247	479	729	1647	3414
1	259	487	732	1651	3414

Table S2 Vibrational modes and frequencies of water in urea solutions.

concentration / M	L1 / cm^{-1}	L2 / cm^{-1}	HOH bend / cm^{-1}	OH stretch / cm^{-1}
0	482	718	1650	3419
0.1	476	715	1650	3419
0.5	479	715	1648	3420
1	480	718	1647	3421

References

[S1] Korepanov, V.; Yu, C.-C.; Hamaguchi, H., Hyper-Raman investigation of intermolecular vibrations of water and ice. *J. Raman Spectrosc.* **2018,** *49* (11), 1742–1746.

[S2] Keuleers, R.; Desseyn, H. O.; Rousseau, B.; Alsenoy, C. V., Vibrational Analysis of Urea. *J. Phys. Chem. A* **1999,** *103* (24), 4621-4630.