Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Structure and energetics of hydrogen bonding networks in dilute HOD/H_2O solutions confined in silica nanopores

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S1. Raman spectroscopy of bulk and nanoconfined HOD/H_2O solutions

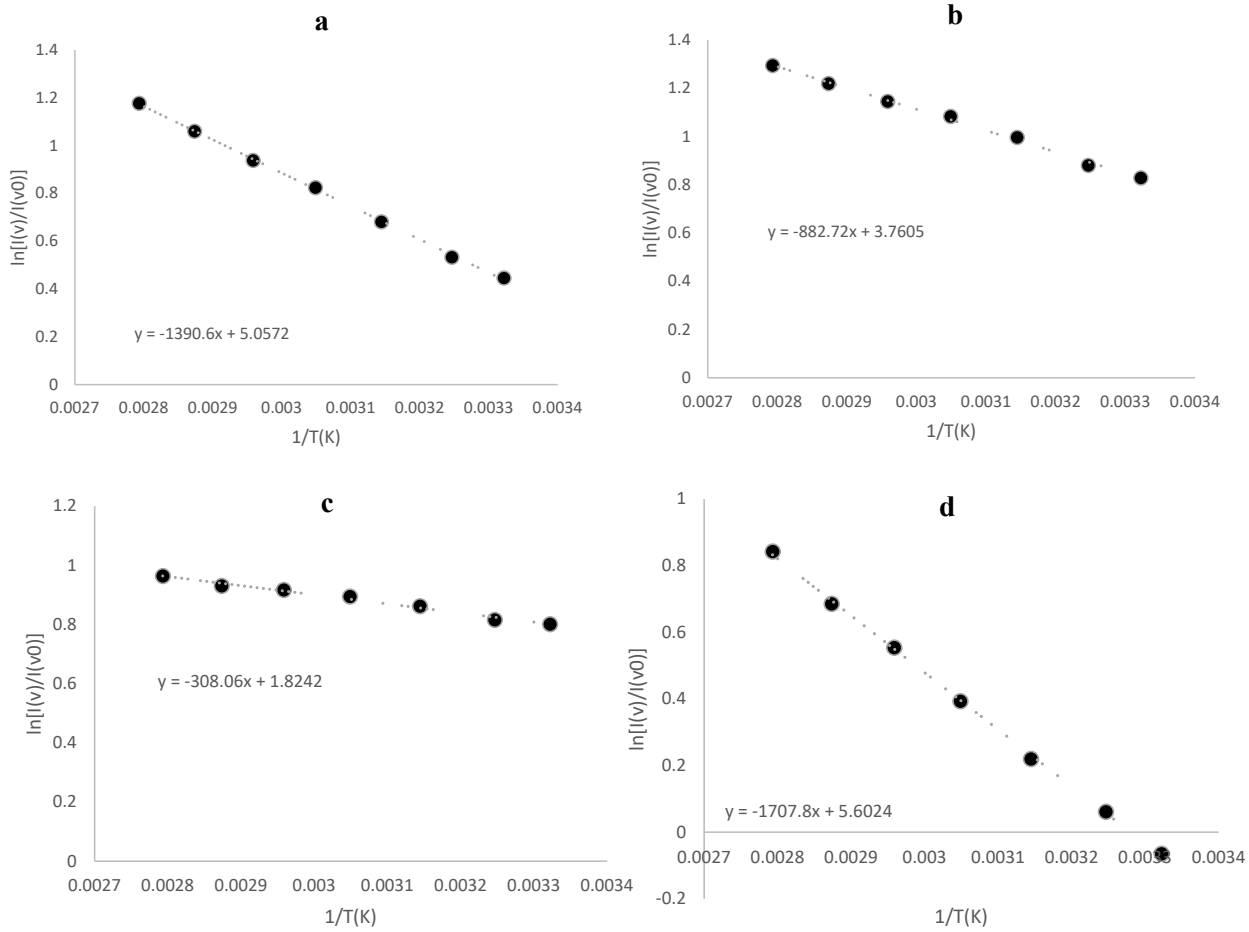

Figure S1. linear plots for ln(Iv/Iv_0) vs $1/T$ used to construct the effective internal energy plots. (a) for Raman shift 2602 cm^{-1}; (b) for Raman shift 2551 cm^{-1}; (c) for Raman shift 2500 cm^{-1}; (d) for Raman shift 2650 cm^{-1}.

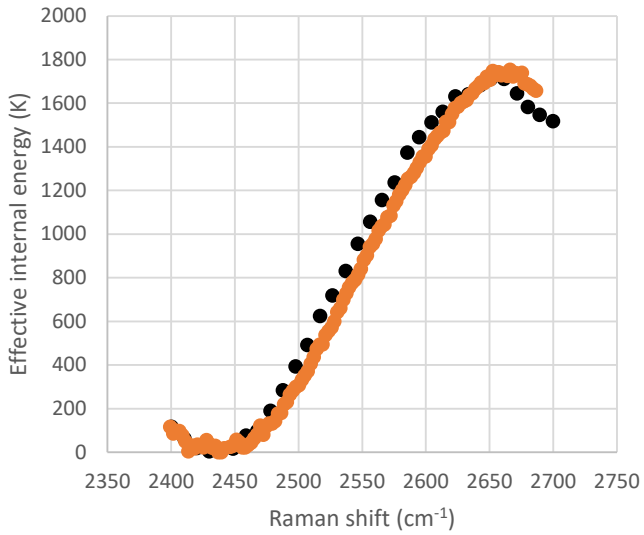

Figure S2. Comparison of the published[1] data on bulk HOD/H_2O solutions with our new data on frequency-dependent internal OD energies. We are in excellent agreement with published work. The effective internal energy of an OD bond as a function of its vibrational frequency (in Kelvin) for dilute HOD/H_2O solutions. Black data points is data from Hare and Sorenson[1]; orange data points that are closely-spaced is the data collected in this study.

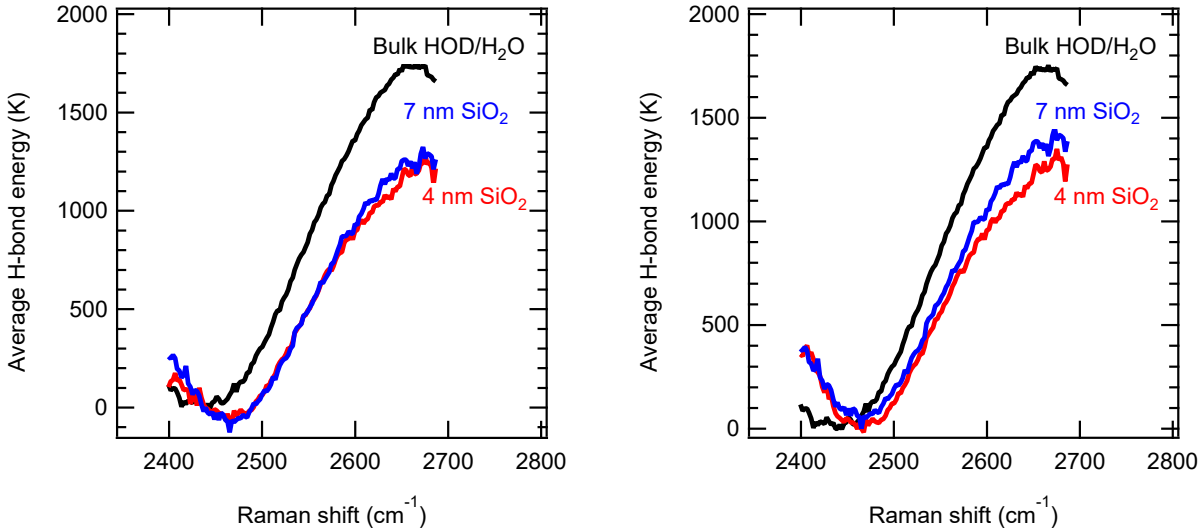

Figure S3. The effective internal energy of an OD bond as a function of its vibrational frequency (in Kelvin) for dilute HOD/H_2O solutions. (Left) Intensities normalized by the Intensity at ν_0 at 2440 cm^{-1}; (Right) Intensities normalized by the Intensity at ν_0 at 2465 cm^{-1}. The Raman shift value of ~ 25 cm^{-1} towards higher frequency remain consistent between the two reference states.

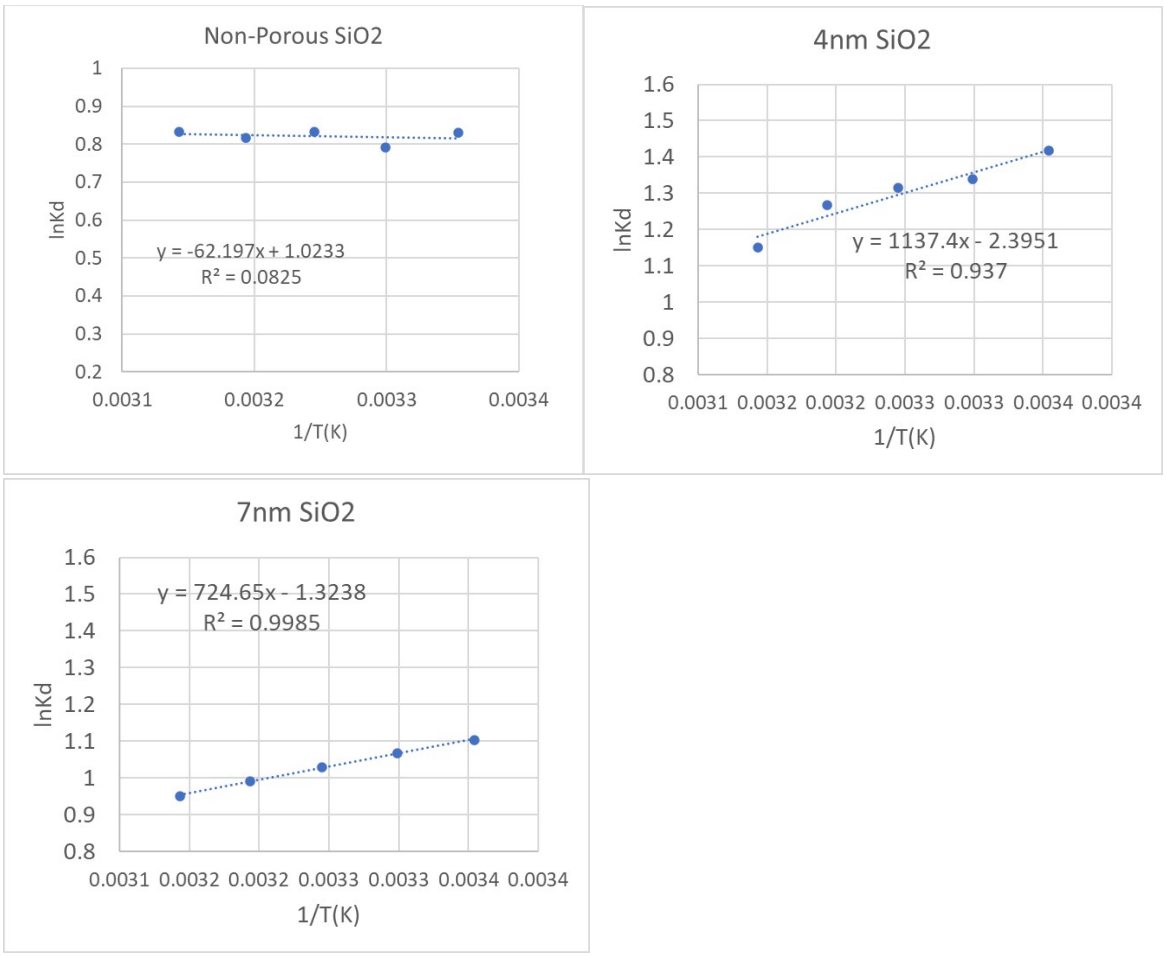

Figure S4. The lnKd vs.1/T plot for non-porous SiO2.

S2. Classical Molecular Dynamics Simulations

The proposed silica-DDEC force field charges and Lennard-Jones parameters. ([a] In interactions with other silica atoms, [b] In interactions with water molecules)

	Atom type	q(e)	σ(Å)	ε(kcal/mol)
Framework sites	Si[a]	1.86	2.7	0.0001
	Si[b]	1.86	3.0	0.01
	O[a]	-0.93	2.7	0.4668
	O[b]	-0.93	3.3	0.1852
Silanols	O(H)	-0.898	3.3	0.1852
	H(O)	0.433	0.0	0.0
Deprotonated Sites	Si(O^-)	1.655	2.7	0.0001
	O^-	-1.08	3.3	0.1852
	O(SiO^-)	-0.99	2.7	0.4668

Reference

1 Hare, D. & Sorensen, C. Raman spectroscopic study of dilute HOD in liquid H2O in the temperature range− 31.5 to 160 C. *The Journal of chemical physics* **93**, 6954-6961 (1990).