Supporting information for: Disentangling Coupling Effects in the Infrared Spectra of Liquid Water

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IR OH-stretch lineshapes for various isotopic solutions

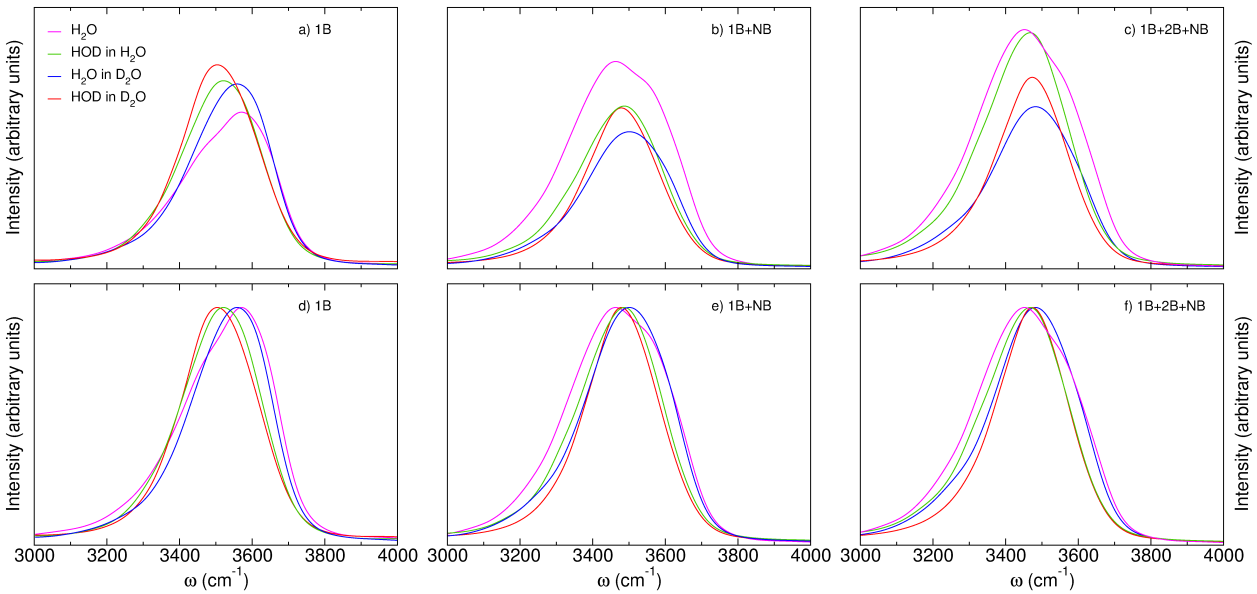

Figure S1: IR OH-stretch lineshapes calculated from CMD simulations of neat H_2O (pink), diluted HOD in H_2O (green), diluted H_2O in D_2O (blue), and diluted HOD in D_2O (red). For each isotopic solution, the OH-stretch lineshape is calculated using the 1B (a and d), 1B+NB (b and e), and 1B+2B+NB (c and f) hierarchy of approximations to the dipole moment (see main text for details). In the top row, all lineshapes are on the same intensity scale (1B spectra are magnified 9 times to facilitate the comparison) and are normalized to the number of OH oscillators of the "solute" molecule. In the bottom row, the intensity maximum of each lineshape is set to 1.

IR OD-stretch lineshapes for various isotopic solutions

CMD simulations analogous to those discussed in the main text for the IR OH-stretch lineshape are performed to characterize coupling effects that modulate the IR OD-stretch lineshape. In this analysis, we consider four isotopic solutions (neat D_2O, diluted HOD in D_2O, diluted D_2O in H_2O, and diluted HOD in H_2O) with different degrees of intramolecular and intermolecular couplings, as depicted in Fig. 1 of the main text with H and D atoms interchanged. Within each solution, we focus our analysis on the OD stretch vibrations; for neat D_2O, we investigate both intramolecular and intermolecular couplings (Fig. 1a), for HOD in D_2O, we specifically monitor the OD vibrations of the "solute" HOD molecules which are intermolecularly coupled to the OD vibrations of the "solvent" D_2O molecules (Fig. 1b), for D_2O in H_2O, we consider the OD stretches of the "solute" D_2O molecules which are intramolecularly coupled but completely decoupled from the OH vibrations of the solvent H_2O molecules (Fig. 1c), and for HOD in H_2O, we investigate the uncoupled OD vibrations of the "solute" HOD molecule (Fig. 1d).

The IR lineshapes calculated from CMD simulations of neat D_2O and diluted HOD in H_2O solutions are compared with the corresponding experimental spectra in Fig. S2.

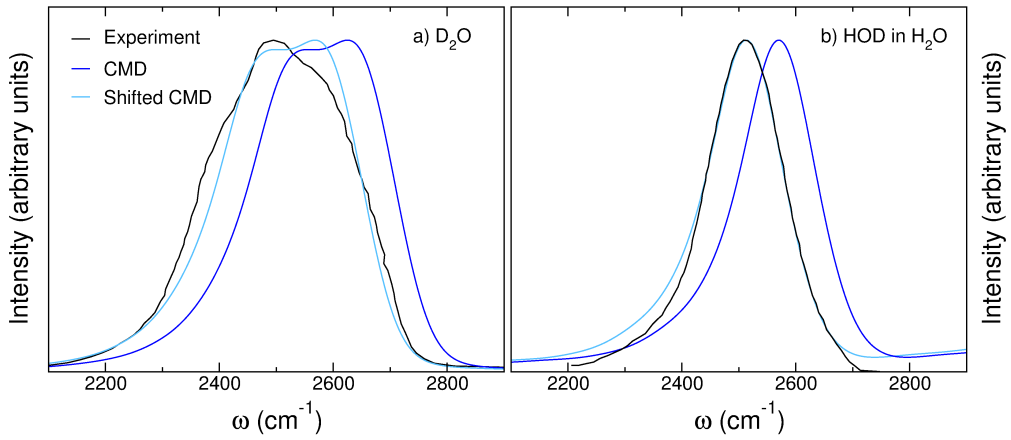

Figure S2: IR OD-stretch lineshapes (blue traces) calculated from CMD simulations of neat D_2O (a) and diluted HOD in H_2O (b) solutions compared with the corresponding experimental results (black traces) from Refs. S1 and S2, respectively. Also shown are the CMD lineshapes (light blue) red-shifted by 57 cm^{-1} to facilitate comparisons with the experimental results.

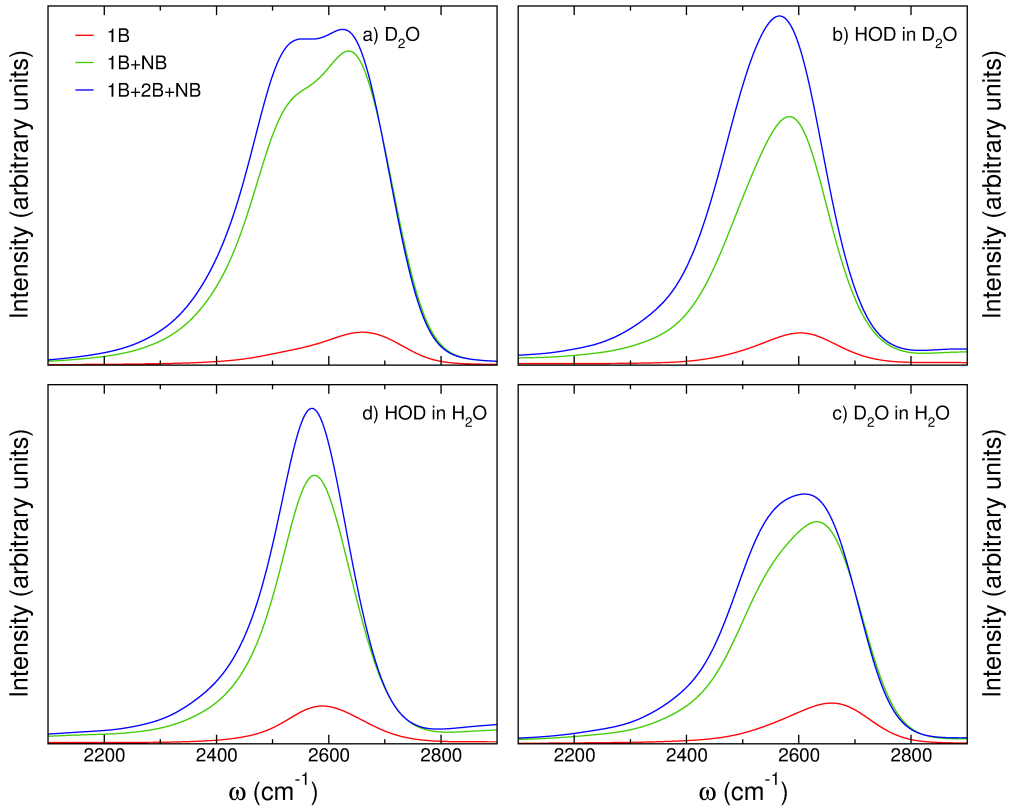

Figure S3: IR OD-stretch lineshapes calculated from CMD simulations of neat D_2O (a), diluted HOD in D_2O (b), diluted D_2O in H_2O (c), and diluted HOD in H_2O (d). For each isotopic solution, the OD-stretch lineshape is calculated using the 1B (red traces), 1B+NB (green traces), and 1B+2B+NB (blue traces) hierarchy of approximations to the dipole moment (see main text for details). All lineshapes are on the same intensity scale and are normalized to the number of OD oscillators of the "solute" molecule.

Table S1: Full-width at half maximum (fwhm) and frequency of maximum absorbance (fma) of the OD-stretch of isotopic solutions.

	1B		1B+NB		1B+2B+NB	
	fwhm	fma	fwhm	fma	fwhm	fma
D_2O	193	2659	264	2636	276	2626
HOD in D_2O	175	2602	197	2582	207	2566
D_2O in H_2O	184	2659	230	2632	243	2609
HOD in H_2O	165	2589	163	2576	166	2579

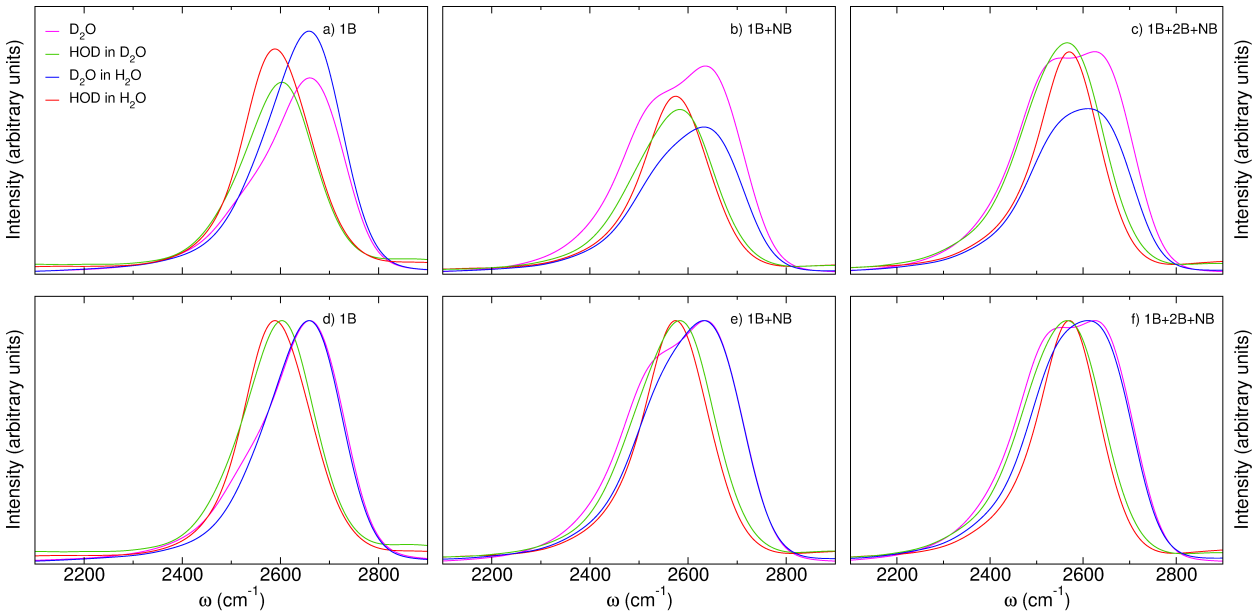

Figure S4: IR OD-stretch lineshapes calculated from CMD simulations of neat D_2O (pink), diluted HOD in D_2O (green), diluted D_2O in H_2O (blue), and diluted HOD in H_2O (red). For each isotopic solution, the OH-stretch lineshape is calculated using the 1B (a and d), 1B+NB (b and e), and 1B+2B+NB (c and f) hierarchy of approximations to the dipole moment (see main text for details). In the top row, all lineshapes are on the same intensity scale (1B spectra are magnified 9 times to facilitate the comparison) and are normalized to the number of OH oscillators of the "solute" molecule. In the bottom row, the intensity maximum of each lineshape is set to 1.

References

(S1) De Marco, L.; Ramasesha, K.; Tokmakoff, A. Experimental Evidence of Fermi Resonances in Isotopically Dilute Water from Ultrafast Broadband IR Spectroscopy. *J. Phys. Chem. B* **2013**, *117*, 15319–15327.

(S2) Asbury, J. B.; Steinel, T.; Stromberg, C.; Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L.; Fayer, M. D. Water Dynamics: Vibrational Echo Correlation Spectroscopy and Comparison to Molecular Dynamics Simulations. *J. Phys. Chem. A* **2004**, *108*, 1107–1119.