Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Structure and dynamics of water molecules confined in triglyceride oils

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This supplementary information contains several figures that illustrate observations made in the main article.

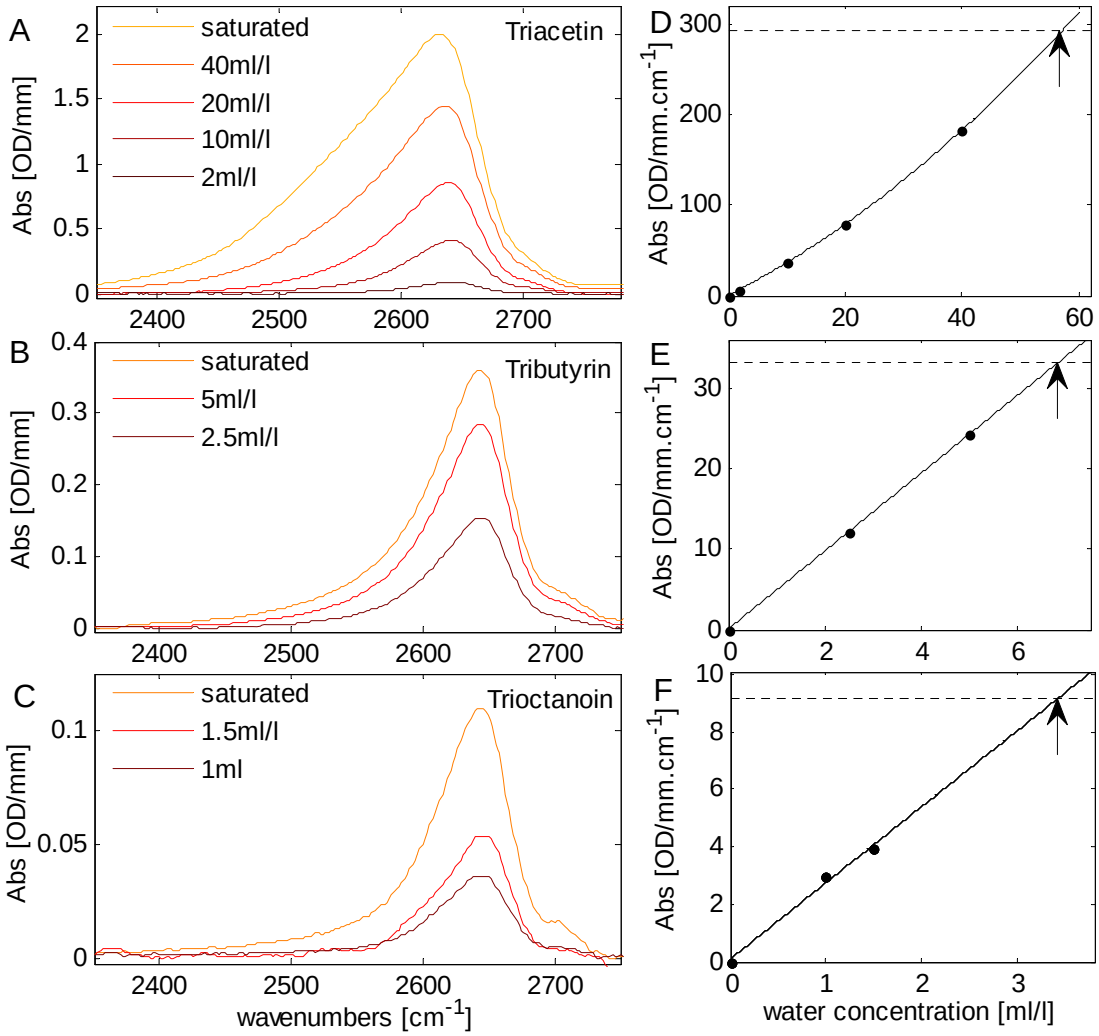

Fig. S1 Linear absorption spectra of different amounts of isotopically diluted water (1:9 D_2O:H_2O) dissolved in triacetin (A), tributyrin (B) and trioctanoin (C), and the integrated OD stretch absorption as a function of water concentration for each triglyceride (D-F). The spectra are corrected for the response of H_2O in triglyceride at the same water concentrations. The integrated OD stretch absorption increases gradually, until the saturation limit is reached and adding more water does not increase the absorption further. For unsaturated solutions, the integrated absorption can be related to the water concentration by an empirical second order polynomial fit (solid lines). The water concentration at which the fit reaches the integrated OD stretch absorption of a saturated solution (dotted lines), indicated with arrows, is then an estimate for the water concentration of a saturated solution. This is 57±2 ml/l, 6.8±1 ml/l and 3.4±1 ml/l for triacetin, tributyrin and trioctanoin respectively, which corresponds to molar water to lipid ratios of about 1:1.7, 1:9, and 1:11.

Table 1 Extracted parameters from Gaussian fit to the linear absorption spectra of water dissolved in triacetin, tributyrin and trioctanoin. The parameters include the amplitude A, center frequency ω and full width at half maximum FWHM. The subscripts refer to the different bands: the H-bonded OD stretch (B) and the free OD stretch (Free) from water molecules that form a single strong H-bond to the triglyceride, and the OD stretch from water molecules that form two weaker H-bonds to the triglyceride (DB), subdivided into symmetric (DB,s) and antisymmetric (DB,a) OD stretch vibrational bands. For water in triacetin, an additional Gaussian band is added to describe the overtone of the bend vibration (Over).

	Triacetin 10% D_2O:H_2O	Tributyrin 10% D_2O:H_2O	Trioctanoin 10% D_2O:H_2O
A_B [mOD]	122	24.8	7.12
A_{DB} [mOD]	117	51.8	13.6
A_{Free} [mOD]	3.73	4.72	2.29
ω_B [cm^{-1}]	2573	2603	2612
ω_{DB} [cm^{-1}]	2634	2642	2645
ω_{Free} [cm^{-1}]	2716	2715	2714
$FWHM_B$ [cm^{-1}]	162.3	133	94.1
$FWHM_{DB}$ [cm^{-1}]	66.2	53.3	50.7
$FWHM_{Free}$ [cm^{-1}]	19.5	32.0	49.6
	Triacetin D_2O	Tributyrin D_2O	Trioctanoin D_2O
A_B [mOD]	874	204.9	46.0
$A_{DB,s}$ [mOD]	59.6	198.4	76.7
$A_{DB,a}$ [mOD]	1164	446.6	141.1
A_{Free} [mOD]	185	186.8	30.1
A_{Over} [mOD]	132	-	-
ω_B [cm^{-1}]	2582	2602	2605
$\omega_{DB,s}$ [cm^{-1}]	2595	2599	2603
$\omega_{DB,a}$ [cm^{-1}]	2686	2698	2707
ω_{Free} [cm^{-1}]	2715	2715	2715
ω_{Over} [cm^{-1}]	2394	-	-
$FWHM_B$ [cm^{-1}]	174.5	170.6	147.2
$FWHM_{DB,s}$ [cm^{-1}]	19.7	34.5	34.7
$FWHM_{DB,a}$ [cm^{-1}]	59.9	52.4	55.1
$FWHM_{Free}$ [cm^{-1}]	25.7	32.7	30.0
$FWHM_{Over}$ [cm^{-1}]	111.7	-	-
	Triacetin H_2O	Tributyrin H_2O	Trioctanoin H_2O
A_B [mOD]	1361	298.8	79.7
$A_{DB,s}$ [mOD]	727	337.2	115.5
$A_{DB,a}$ [mOD]	1645	742.9	199.1
A_{Free} [mOD]	-	29.2	40.3
A_{Over} [mOD]	0.310	-	-
ω_B [cm^{-1}]	3492	3532	3555
$\omega_{DB,s}$ [cm^{-1}]	3563	3555	3555
$\omega_{DB,a}$ [cm^{-1}]	3633	3643	3648
ω_{Free} [cm^{-1}]	-	3687	3690
ω_{Over} [cm^{-1}]	3265	-	-
$FWHM_B$ [cm^{-1}]	216.9	221.6	216.3
$FWHM_{DB,s}$ [cm^{-1}]	74.0	64.5	58.2
$FWHM_{DB,a}$ [cm^{-1}]	71.0	62.6	58.6
$FWHM_{Free}$ [cm^{-1}]	-	16.6	17.9
$FWHM_{Over}$ [cm^{-1}]	177.7	-	-

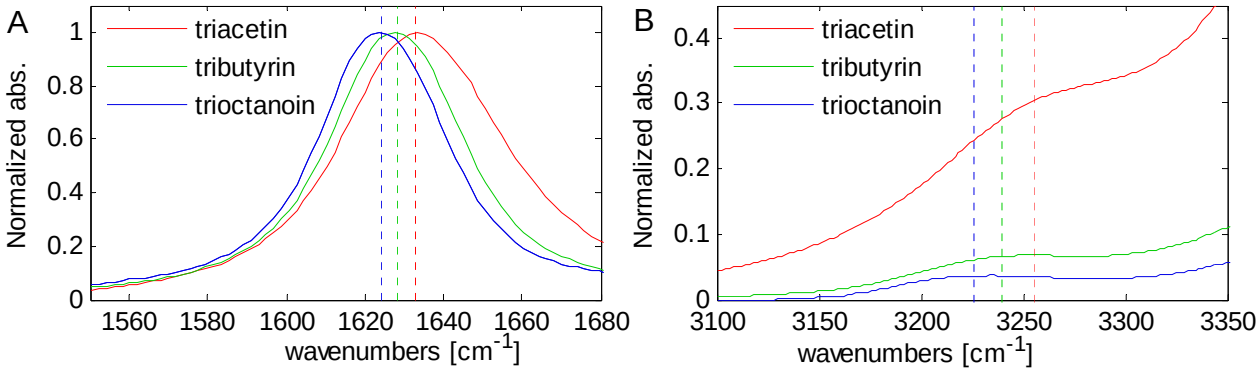

Fig. S2 Linear absorption spectra of saturated solutions of H_2O in triacetin, tributyrin and trioctanoin in the water bend region (A) and at approximately twice the frequency (B). The spectra are corrected for D_2O in triglyceride background and normalized on peak intensity between 1580 and 1680 cm^{-1}. The vertical lines indicate peak positions. Based on the frequency and frequency shift with increasing fatty acid chain length, the small peak around 3240 cm^{-1} can be assigned to the overtone of the bend vibration.

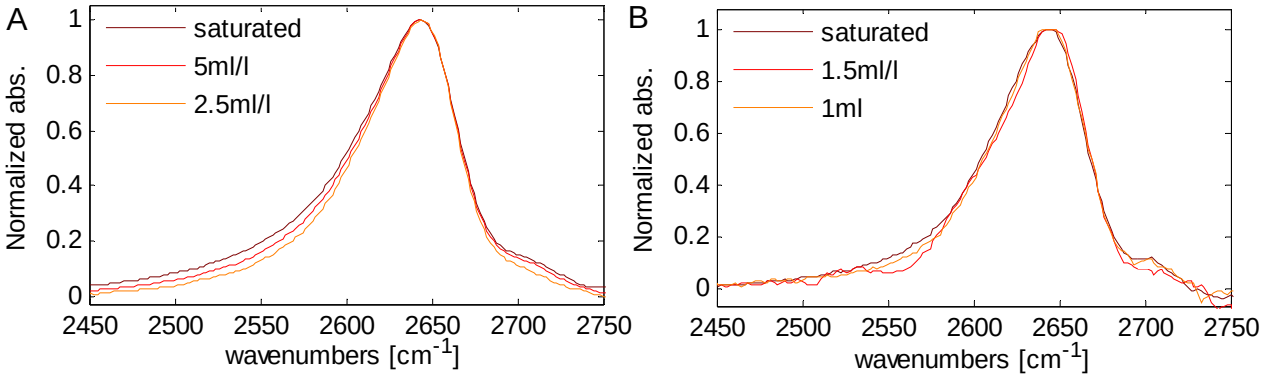

Fig. S3 Linear absorption spectra of isotopically diluted water (10% D_2O:H_2O) dissolved in tributyrin (A) and trioctanoin (B) for different water concentrations. The spectra are corrected for H_2O in triglyceride background and normalized on peak intensity. The spectral shape does not change significantly with the water concentration, indicating that the contribution of water clusters is negligible.

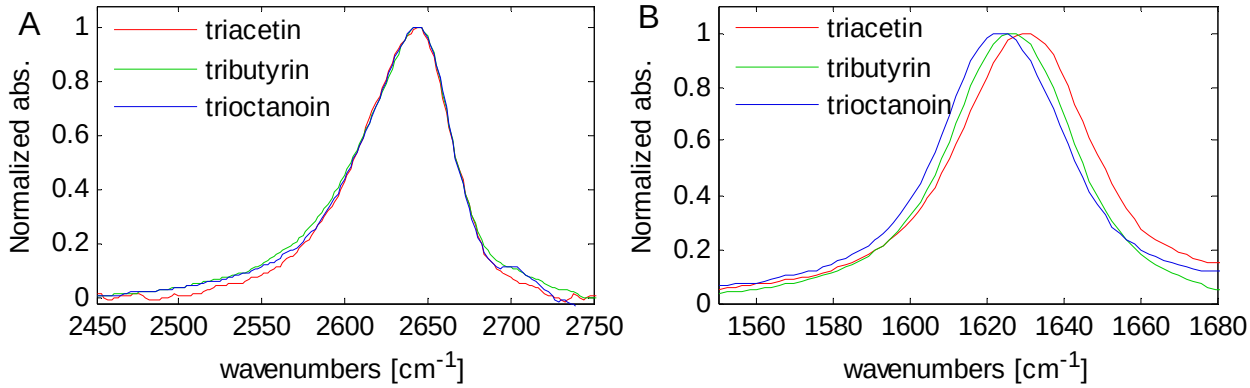

Fig. S4 Linear absorption spectra of isotopically diluted water (10% D_2O:H_2O) (A) and H_2O (B) dissolved in triacetin, tributyrin and trioctanoin at low water concentration (<2.5 ml/l). The spectra are corrected for H_2O (A) and D_2O (B) in triglyceride background and normalized on peak intensity. The spectra are identical within errorbar in the OD stretch region (A) while the water bend vibration still shows a considerable redshift with increasing fatty acid chain length (B).

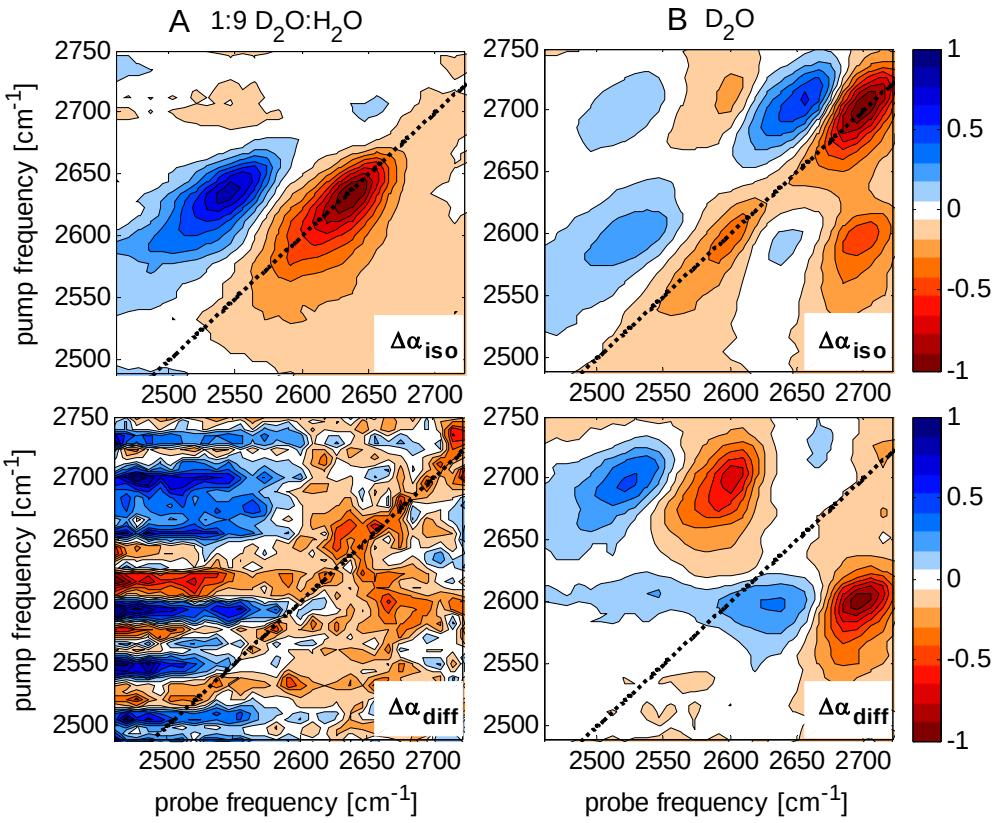

Fig. S5 2DIR spectra of saturated solutions of 1:9 D_2O:H_2O (A) and D_2O (B) in tributyrin, at 0.4 picoseconds after excitation. The top row shows the isotropic 2DIR spectrum ($\Delta\alpha_{iso} = 1/3(\Delta\alpha_{||} + 2\Delta\alpha_{\perp})$, rotation free) and the bottom row the polarization difference 2DIR spectrum ($\Delta\alpha_{diff} = \Delta\alpha_{\perp}(\Delta\alpha_{||,max}/\Delta\alpha_{\perp,max}) - \Delta\alpha_{||}$, cross peaks enhanced). The spectra are normalized on peak intensity.

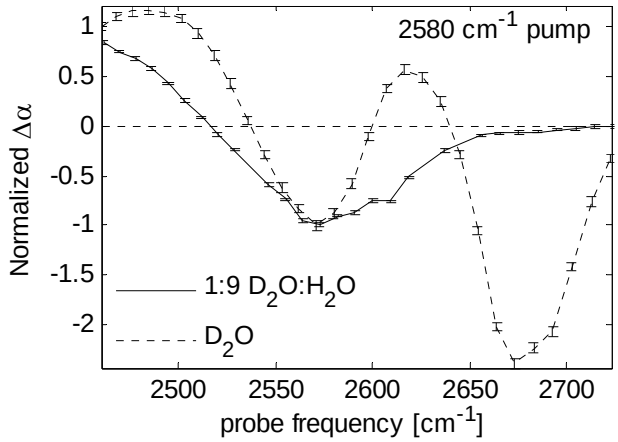

Fig. S6 Crosssections of the isotropic 2DIR spectra at 2580 cm^{-1} pump frequency for 1:9 D_2O:H_2O and D_2O in triacetin, at 0.4 picoseconds after excitation and normalized at 2570 cm^{-1} probe frequency. The cross peak (at probe frequency 2680 cm^{-1}) for 1:9 D_2O:H_2O is approximately 100x smaller than for D_2O.

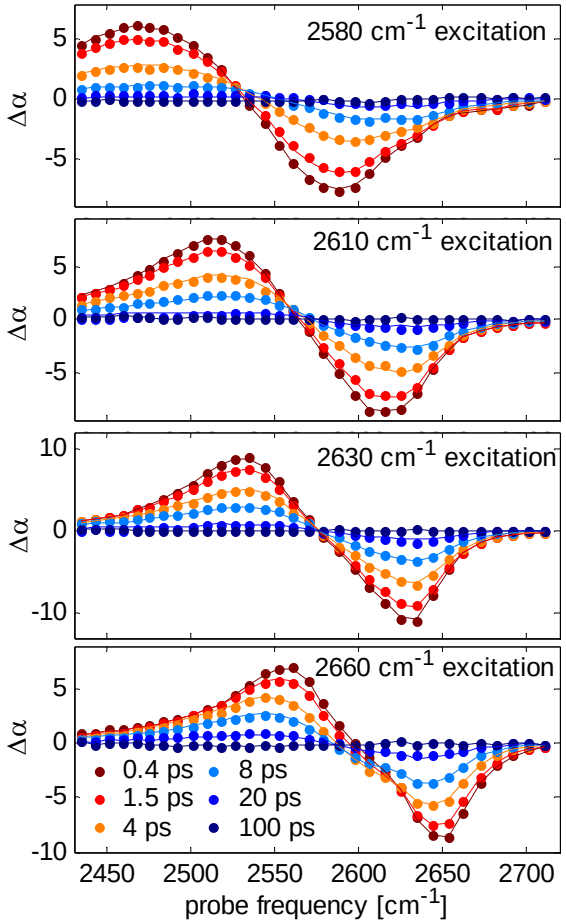

Fig. S7 Slices of the 2DIR spectrum at different excitation frequencies, for a saturated solution of 1:9 D_2O:H_2O in triacetin (solid lines are description with spectral decomposition fit). The colors indicate different ps delay times.

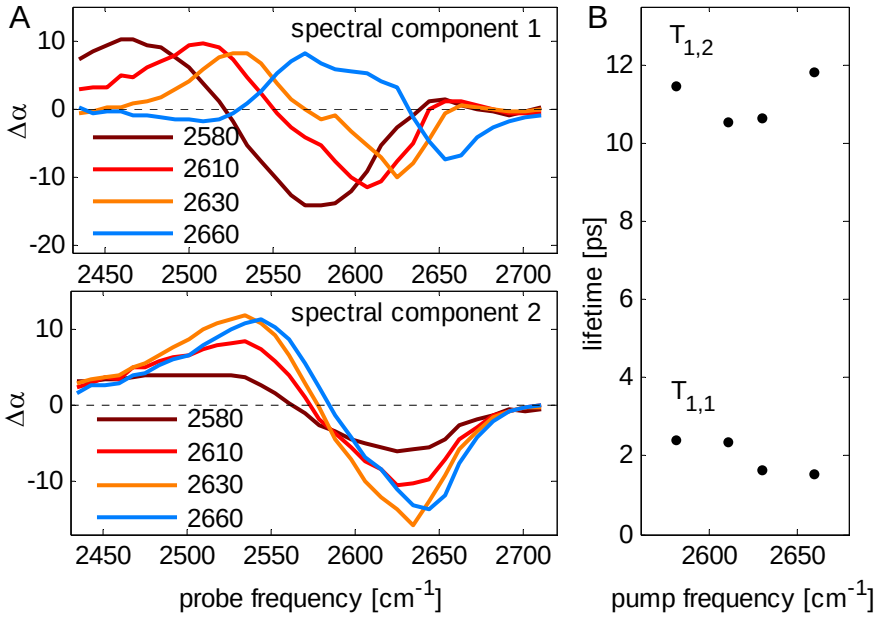

Fig. S8 Spectral components (A) of the 2DIR spectral slices for a saturated solution of 1:9 D_2O:H_2O in triacetin (Fig.S7), and their corresponding lifetimes (B).