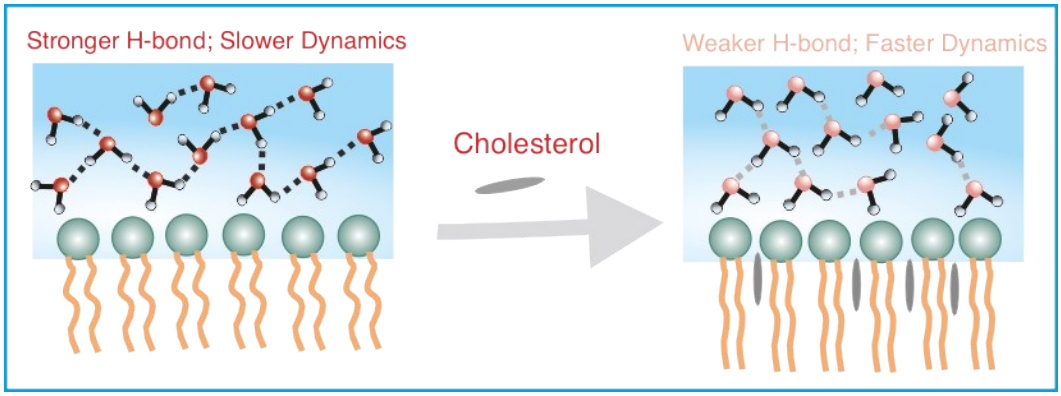
Supporting Information for

Addition of cholesterol alters the hydration at the surface of model lipids: a spectroscopic investigation

Sumana Pyne, Partha Pyne and Rajib Kumar Mitra*

Department of Chemical Biological and Macromolecular Sciences
S N Bose National Centre for Basic Sciences
Block JD, Sector III, Salt Lake, Kolkata 700106, INDIA

* Email: rajib@bose.res.in



Scheme1: Response (structure & dynamics) of wrapped water at lipid-water interface perturbed in presence of cholesterol.

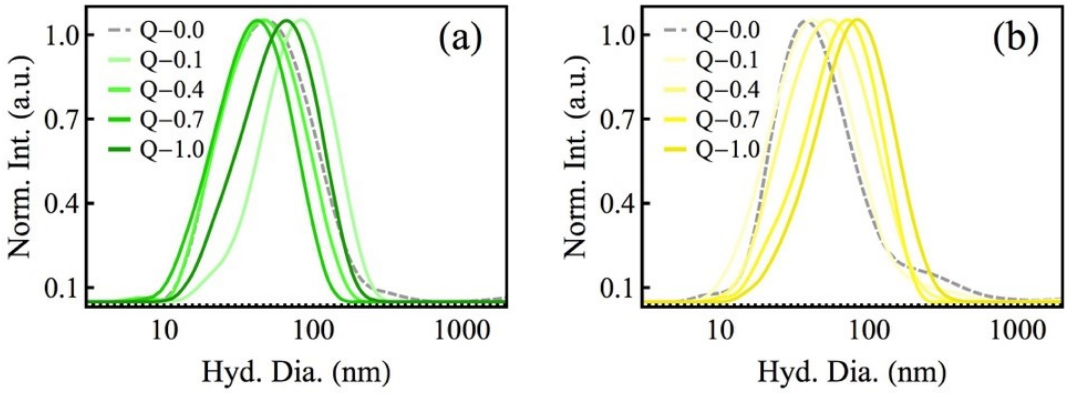


Figure S1. Dynamic Light Scattering profile at different Q-value for (a) DOPG and (b) DOPC/DOPG systems respectively.

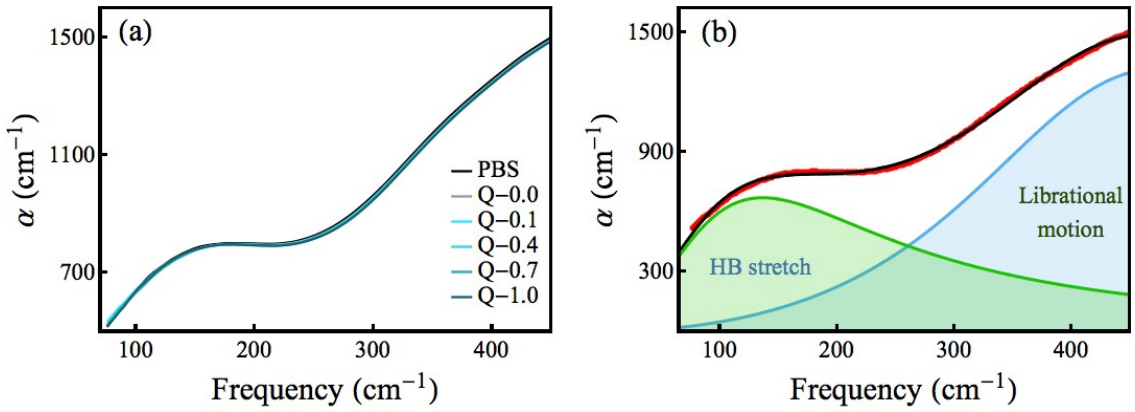


Figure S2. (a) Absorption coefficient as a function of frequency for DOPC liposomes at different Q. (b) Representative fitted profile for water. Red curve shows the raw data of water, black line shows the total fitted data. Blue curve indicated HB-stretch and green curve indicates libration motion of water molecule.

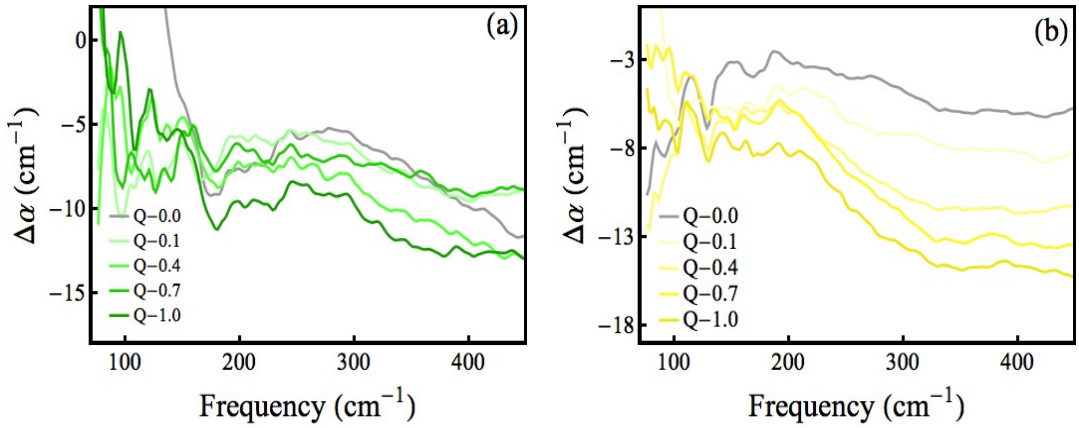


Figure S3. $\Delta\alpha$ as a function of frequency at different Q-value for (a) DOPG and (b) DOPC/DOPG liposomes.

Table S1. Peak frequency of *total hydration* for three liposomes. Data are fitted by using damped harmonic oscillator equation:

DOPC			DOPG			DOPC/DOPG		
Q	$\nu_{HB}(cm^{-1})$	$\nu_{Lib}(cm^{-1})$	**Q**	$\nu_{HB}(cm^{-1})$	$\nu_{Lib}(cm^{-1})$	**Q**	$\nu_{HB}(cm^{-1})$	$\nu_{Lib}(cm^{-1})$
0	112.2 ± 1.1	395.8 ± 3.1	0	189.7 ± 3.1	419.6 ± 0.03	0	117.9 ± 3.4	403.7 ± 0.007
0.1	147.9 ± 2.3	377.6 ± 9.5	0.1	114.6 ± 10.1	408.8 ± 0.02	0.1	126.9 ± 3.4	415.2 ± 0.02
0.4	129.4 ± 2.5	357.5 ± 1.4	0.4	184.4 ± 4.4	422.5 ± 0.14	0.4	119.8 ± 1.9	379.8 ± 0.003
0.7	114.8 ± 0.9	342.4 ± 6.1	0.7	157.5 ± 6.9	434.4 ± 0.26	0.7	132.2 ± 2.6	389.4 ± 0.001
1.0	106.4 ± 1.5	339.9 ± 4.4	1.0	185.7 ± 4.3	392.7 ± 0.02	1.0	100.9 ± 10.9	394.8 ± 0.02

Table S2. Lifetime of oscillator's dipole moment autocorrelation function corresponding to "HB-stretch" and "librational motion" modes of water associated with DOPC, DOPG and DOPC/DOPG systems as a function of Q.

DOPC			DOPG			DOPC/DOPG		
Q	$\tau_{HB}(fs)$	$\tau_{Lib}(fs)$	**Q**	$\tau_{HB}(fs)$	$\tau_{Lib}(fs)$	**Q**	$\tau_{HB}(fs)$	$\tau_{Lib}(fs)$
0	282 ± 22	17 ± 2	0	181 ± 29	35 ± 12	0	147 ± 12	24 ± 2
0.1	407 ± 101	28 ± 2	0.1	61 ± 4	40 ± 5	0.1	157 ± 22	17 ± 3
0.4	278 ± 49	33 ± 3	0.4	34 ± 8	40 ± 11	0.4	155 ± 9	22 ± 0.7
0.7	391 ± 35	33 ± 1	0.7	33 ± 9	34 ± 12	0.7	129 ± 11	23 ± 0.9
1.0	243 ± 79	34 ± 1	1.0	86 ± 8	37 ± 6	1.0	80 ± 9	20 ± 1

Table S3. Peak frequency and lifetime corresponding HB-stretch and librational mode of hydration layer of lipids in absence and in presence of cholesterol (after performing PCA).

	DOPC		DOPG		DOPC/DOPG	
	$Q = 0$	$Q \neq 0$	$Q = 0$	$Q \neq 0$	$Q = 0$	$Q \neq 0$
ν_{HB} (cm^{-1})	112.2	112.6	189.7	166.08	118	105.63
ν_{Lib} (cm^{-1})	395.8	349.9	419.7	428.8	403.7	388.4
τ_{HB} (fs)	282.06	221.7	181.08	46.62	147.2	87.8
τ_{Lib} (fs)	17.67	33	35.6	36.9	24.03	23.09

Table S4. Peak frequency corresponding HB-stretch and librational mode of hydration layer of lipids and the corresponding peak shifts in absence and in presence of cholesterol (after performing PCA)

	DOPC			DOPG			DOPC/DOPG		
	$Q = 0$	$Q \neq 0$	Peak Shift (cm^{-1})	$Q = 0$	$Q \neq 0$	Peak Shift (cm^{-1})	$Q = 0$	$Q \neq 0$	Peak Shift (cm^{-1})
ν_{HB} (cm^{-1})	112.2 ± 1.1	112.6 ± 1.5	0.4	189.7 ± 3.1	166.08 ± 10.4	23.62	118 ± 3.4	105.63 ± 0.4	12.37
ν_{Lib} (cm^{-1})	395.8 ± 3.1	349.9 ± 3.8	45.9	419.7 ± 0.3	428.8 ± 9.6	-9.1	403.7 ± 0.7	388.4 ± 10.3	15.3