Supplementary information

Table 1. Sum up of all vibrational modes

Nr	Vibrational mode	IR (cm^{-1})	SFG (cm^{-1})	Ref.
1	ν_s(C-O-C)	1129	1121	24
2	ν_s(PhO)	1263	1260	25
2	ν(C-N)	1280	1279	25
3	ν_s(N-O)	1341	1341	26
4	ν_a(N-O)	1517	1521	26
5	skl(C=C)	1590	1592	25
6	ν_s(CH)	2856	2857	
7	ν_s(CH)	-	2879	
8	ν_{as}(CH)	-	2887	
9	FR	-	2914	
10	FR	2926	2927	
11	ν_{as}(CH)	2957	2966	
12	aromatic CH	-	3020	37, 39
13	aromatic CH	-	3060	37-39
14	OH ice-like	-	3250	52, 53
15	OH liquid-like	-	3382	52, 53
16	non donor OH against hydrocarbon phase	-	3560	16
17	free OH	-	3700	41, 42

Table 2. Fitting Parameters for NB15C5 4.92mM in SSP polarization conditions:

Fitted peak wavenumbers (cm^{-1})	Amplitude (a.u)	Γ_υ (cm^{-1})
2857	1.06 ± 0.001	8 ± 0.0001
2879	1.02 ± 0.0008	9.5 ± 6e-005
2887	-2.1 ± 0.0005	12.1 ± 3e-005
2914	10.3 ± 0.0002	38.724 ± 3.87
2927	-3.3± 0.00047	8 ± 0.0002
2966	-6.0 ± 0.0001	25.6 ± 4.66
3250	14.57 ± 2.1	97.406 ± 6.11
3382	30.614 ± 3.32	124.12 ± 5.01
3700	-19.28 ± 0.7	69.449 ± 2.36

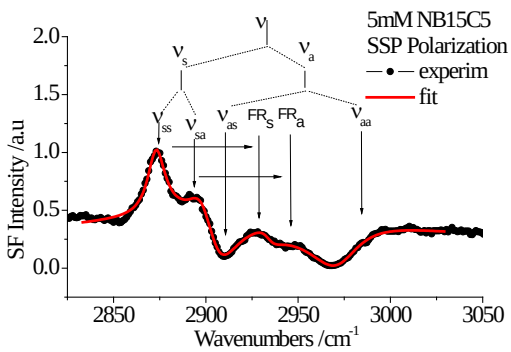

Figure 1. SSP polarization spectra of 5mM NB15C5 showing the diagram of the intermolecular coupling model proposed by Zhelyaskov.

VSFS spectral fit using Zhelyaskov model.

Zhelyaskov[33] proposed a model arguing that the appearance of several features in the CH region of crown ethers might be explained by the splitting of an unperturbed CH stretching ν_u. This is the vibration of a single CH oscillator without any interference of adjacent oscillators. The first effect responsible for splitting this molecular vibration is due to coupling of the two CH oscillators from the CH_2 unit resulting in a splitting of the unperturbed vibration ν_u into ν_s – symmetric and ν_a – asymmetric. The second interaction is a coupling between every adjacent CH_2 resulting in a further splitting of ν_s – symmetric into ν_{ss} – symmetric in – phase and ν_{sa} – symmetric out – of – phase and splitting of ν_a – asymmetric into ν_{as} – asymmetric in – phase and ν_{aa} – asymmetric out – of – phase The last interaction is a Fermi resonance between the symmetric split vibrations ν_{ss} and ν_{sa} with the overtone of the CH bending modes which appear in this region and increase the separation between the ν_{ss} and ν_{sa} modes. Thus the spectra end up with six different vibration modes: FR_s, ν_{ss}, ν_{sa}, FR_a, ν_{as} and ν_{aa}, where FR_s and FR_a are the symmetric and asymmetric Fermi resonances, respectively, as shown in Figure 1