Supporting Information

Effects of Sulfation and Environment on Structure of Chodroitin Sulfate Studied by Raman Optical Activity

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Table S1 Raman and ROA frequencies of chondroitin sulfate and its basic monosaccharide units.

C4S Raman	C4S ROA	C6S Raman	C6S ROA	GlcA Raman	GalNAc-4S Raman	GalNAc-6S Raman	Assignment
1648 (m)		1648 (m)			1642 (m)	1641 (m)	Amide I (GalNAc)
1595 (w)		1595 (w)		1595 (w, br)			COO^- asymmetric deformation (GlcA)
1461 (w)		1461 (m)			1462 (m)	1455 (m)	CH_2 deformation (GalNAc)
1415 (s)	1425 (-m)	1414 (s)	1426 (-m)	1416 (s)			COO^- symmetric deformation (GlcA)
1378 (s)	1377 (+s)	1380 (s)	1379 (+s)		1380 (s)	1382 (s)	CH_3 symmetric deformation (GalNAc)
				1362 (s)			CH bending deformations (GlcA)
1343 (s)	1357 (+s) / 1332 (-m)	1343 (s)	1360 (+s) / 1335 (-m)		1331 (s)	1328 (s)	Amide III (GalNAc)
1303 (sh)	1300 (-m)	1303 (sh)	1298 (-m)	1302 (m)			C(5)H bending deformation (GlcA)
1270 (m, br)	1262 (+m)	1274 (m)	1269 (+s)		1271 (s)	1276 (s)	OSO_3^- asymmetric stretch (partially)
1239 (sh)	1238 (+m)	1240 (sh)	1236 (+sh)	1240 (w)			
					1225 (sh)	1223 (sh)	
1205 (w)		1206 (w)		1204 (w)			
1159 (m)	1159 (+m)	1162 (m)	1165 (+m)	1152 (m)		1152 (m)	COH, and CH deformations
1135 (sh)	1133 (-s)				1141 (m)		
	1117 (-s)	1135 (w)	1142 (-w)	1118 (s)		1127 (w)	
		1098 (w)	1107 (-s) / 1089 (+s)			1094 (w)	
1081 (s)	1089 (+s) / 1073 (-m)				1082 (vs)		OSO_3^- symmetric stretch
		1065 (vs)		1061 (s)		1065 (vs)	
1052 (s)	1052 (-m)				1050 (s)		
		1035 (sh)				1032 (m)	
1029 (sh)	1027 (+w)			1040 (s)	1016 (s)		
	1007 (-m)	999 (w)	1007 (+m)			998 (s)	C-O-S stretch, partly COH and CH deformations
		983 (sh)	983 (+m)			980 (sh)	
978 (m)	973 (+m)				973 (s)		
940 (m)	913(+w)/937 (-m)	940 (m)	913(+w)/939 (-m)				C-O-C linkage vibration
891 (w)		888 (m)			895 (w)	881 (sh)	
862 (m)	865 (+w)	864 (w)			864 (m)	855 (m)	
	818 (+w)	831 (m)			830 (w)	832 (sh)	
803 (w)				801 (w)		803 (m)	C-O-S deformations + skeletal modes
	764 (-w)		764 (+w)		760 (s)		
725 (m)		725 (w)				716 (m)	
641 (w, br)	661 (-m)		661 (-m)				
		640 (m)		622 (w)	631 (m)	621 (m)	
593 (w, br)	603 (-m)	581 (m)	604 (-m, br)		603 (m)	591 (m)	
552 (w, br)	545 (+m)		532 (+m)	576 (m)	562 (m)	533 (m)	
	500 (-w)		504 (-w)		517 (w)	495 (w)	
	465 (+m)	469 (sh)		460 (s)	436 (sh)	441 (m)	skeletal modes
420 (w, br)	423 (-w)	416 (m)	427 (-w)	417 (s)	416 (m)	418 (m)	
	397 (+vs)		387 (+m, br)				
377 (m)		376 (w)					
339 (m)	343 (+w)			343 (m)	368 (w)	361 (w)	
	306 (-sh)	335 (w, br)	319 (-m)		323 (w)	315 (w)	
293 (m)	279 (-s, br)	281 (m, br)	251 (-m, br)	290 (sh)	271 (w)	282 (w)	

C4S, chondroitin 4-sulfate; C6S, chondroitin 6-sulfate; GalNAc-4S, N-acetyl-galactosamine 4-sulfate; GalNAc-6S, N-acetyl-galactosamine 6-sulfate; GlcA, D-glucuronic acid; (s), strong; (m), medium; (w), weak; (sh), shoulder; (br), broad; (vs), very strong; (+), positive; (-), negative; … / …, couplet.

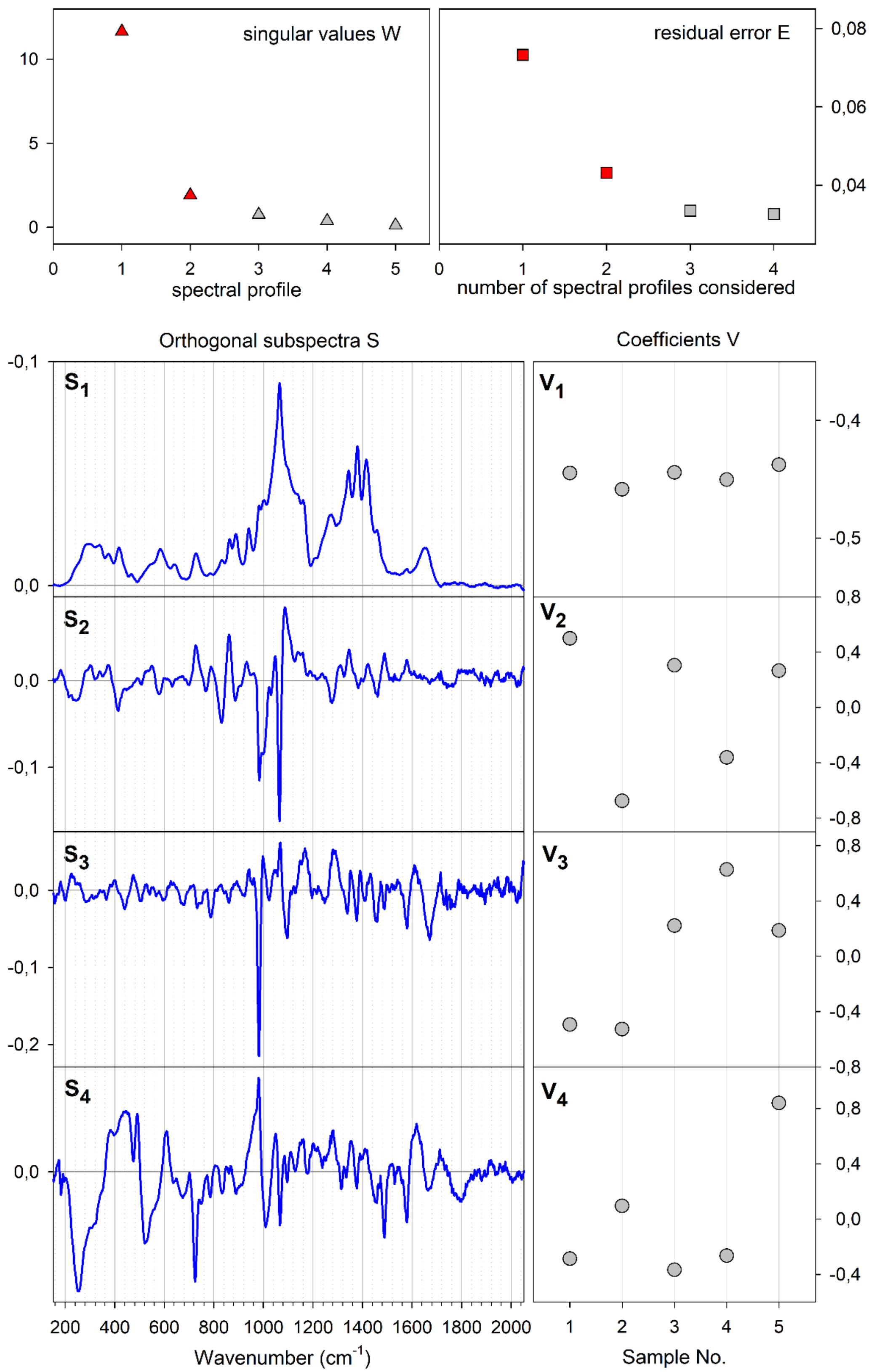

Fig. S1 The factor analysis of Raman spectra of different CS samples (see Table 1 for identification).

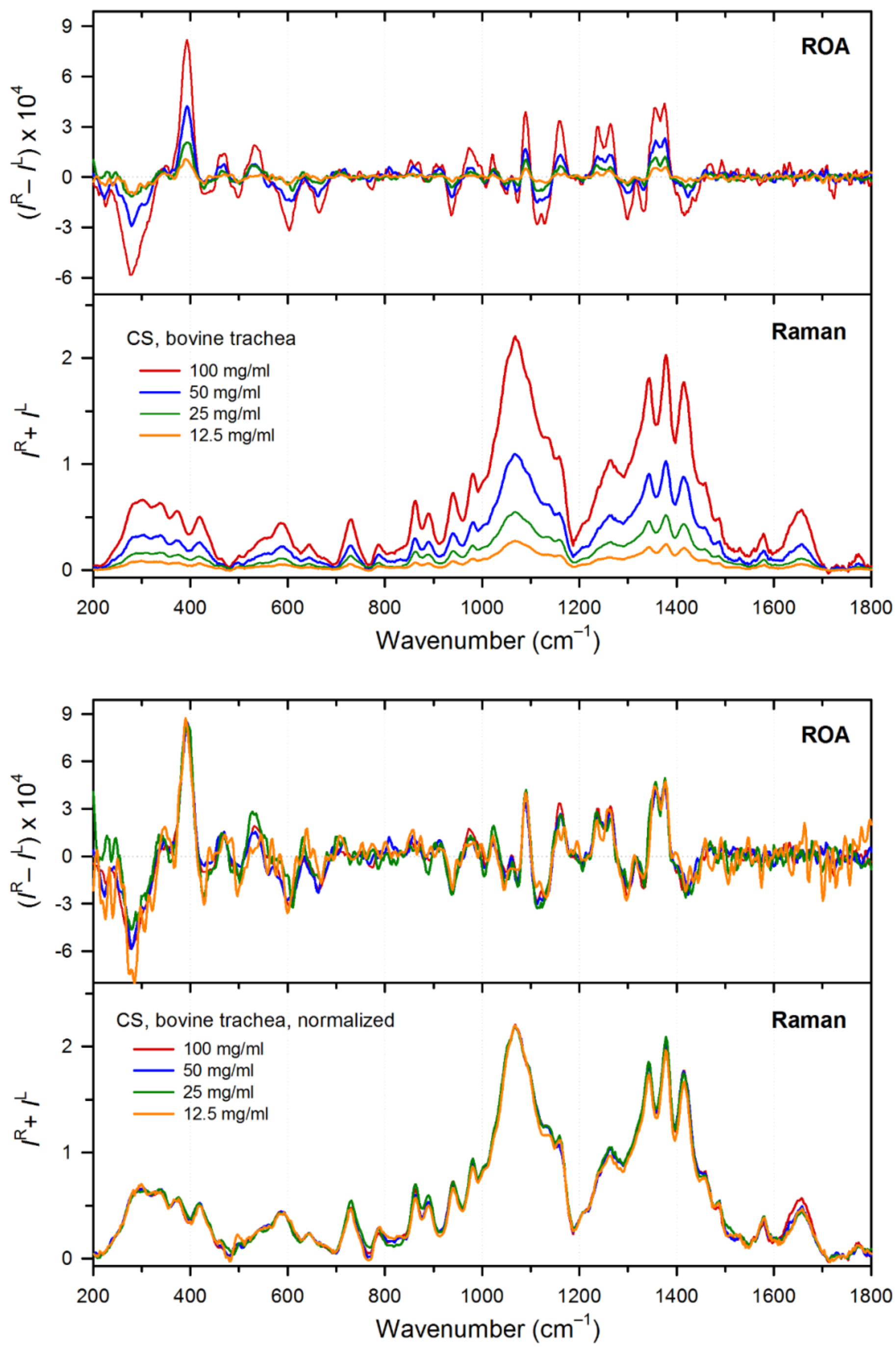

Fig. S2 Raman and ROA spectra of CS sodium salt from bovine trachea (1) at various concentrations. The upper panels show spectra normalized on the same accumulation time; the lower panels display spectra normalized on the same integral intensity (using Raman spectrum in 500 - 1700 cm^{-1} interval).

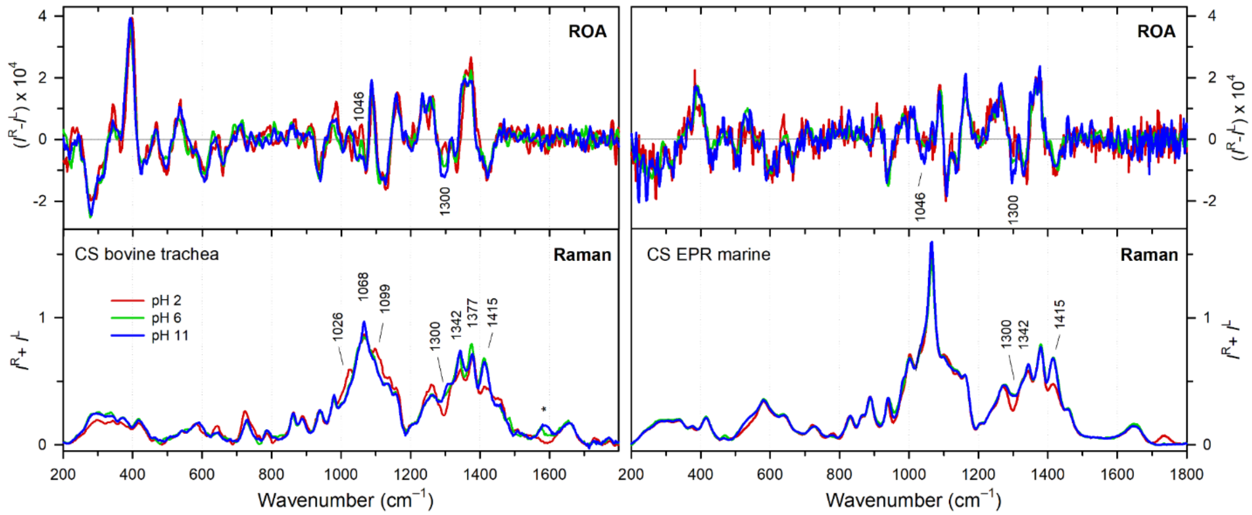

Fig. S3 Raman and ROA spectra of CS from bovine trachea (left) and CS EPR marine (right) at neutral (pH 6, green), basic (pH 11, blue), and acidic (pH2, red) environment. The major changes in spectra are labelled. The band at 1590 cm^{-1} corresponding to sample's impurities is marked by asterisk.

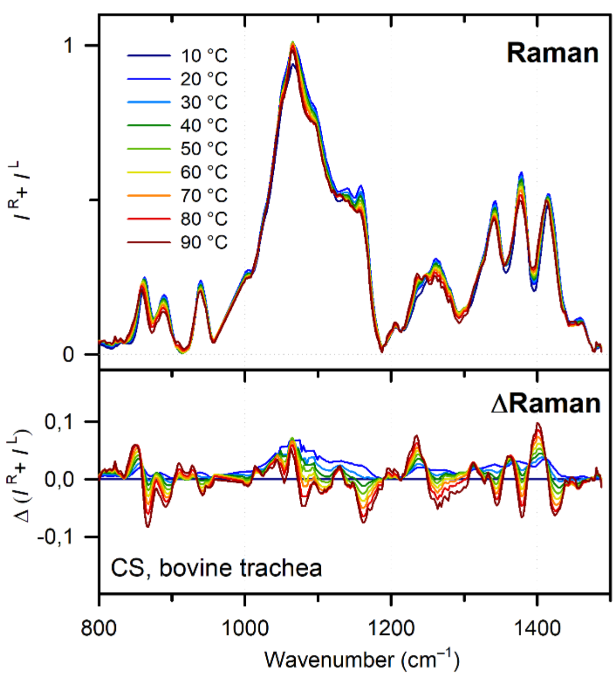

Fig. S4 Raman and difference (vs. 10°C) Raman spectra of CS from bovine trachea measured at various temperatures.

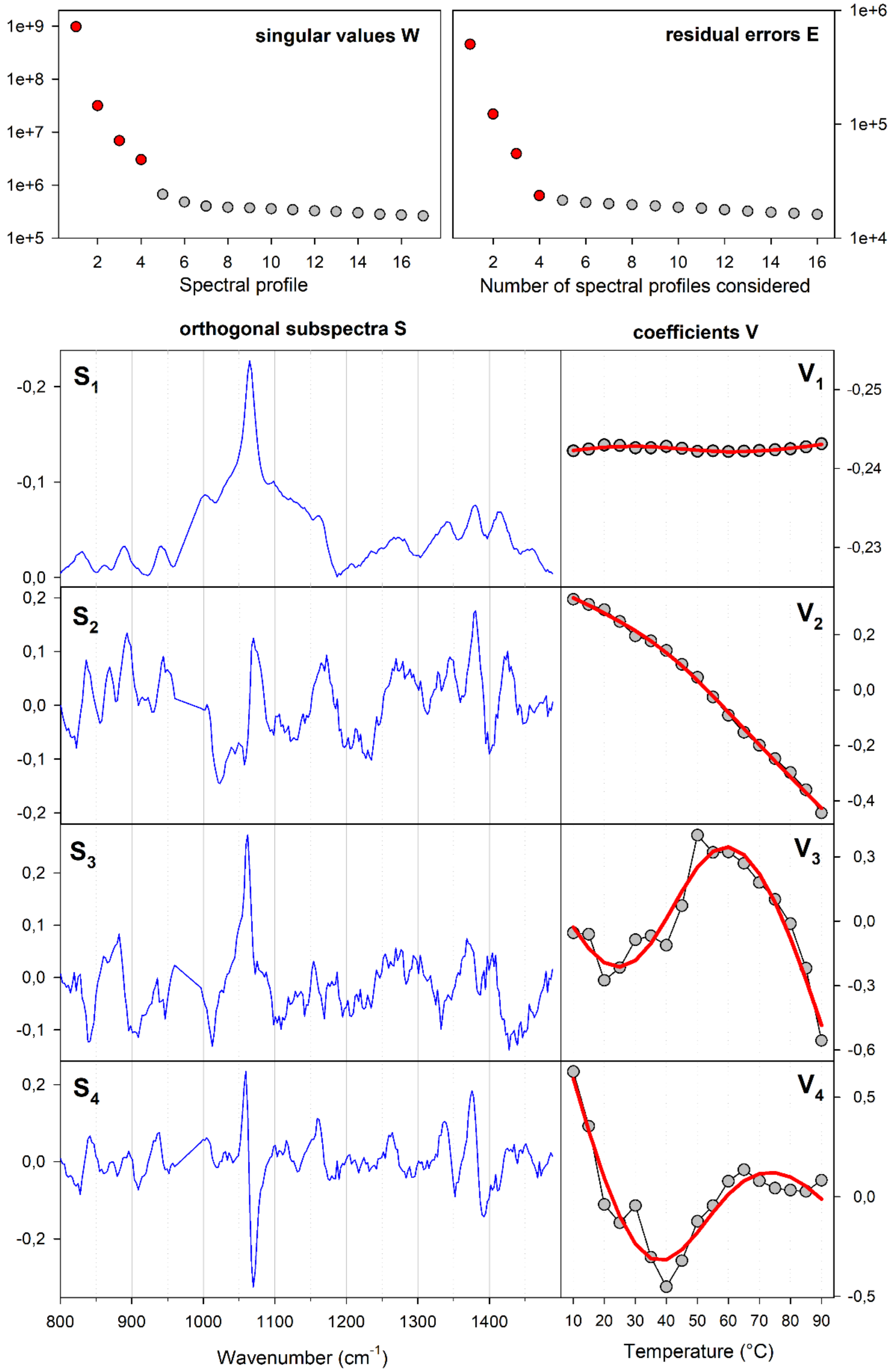

Fig. S5: The factor analysis of Raman spectra temperature dependence of CS EPR marine. Result of the one-step transition fit is shown by red lines.

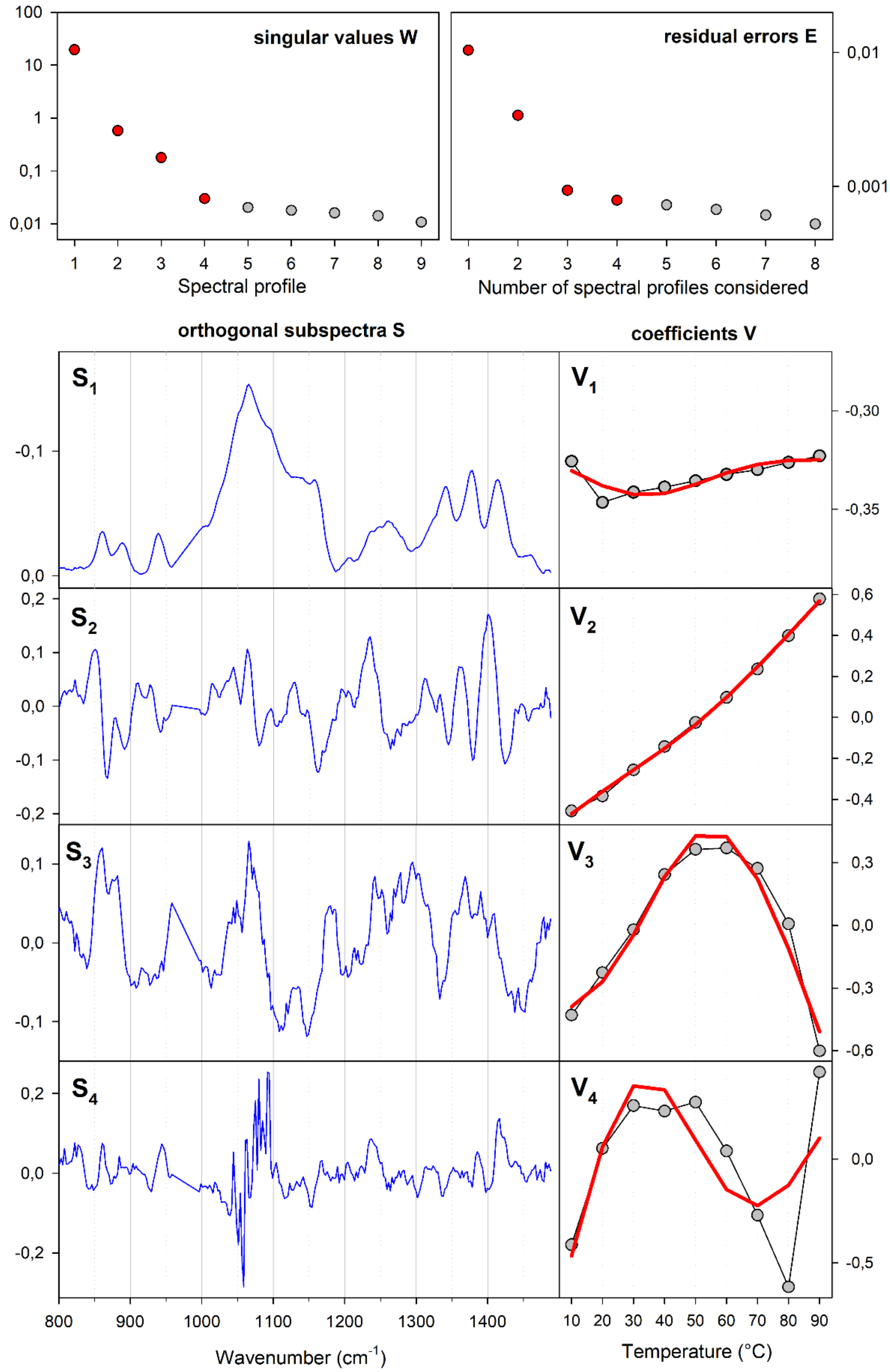

Fig. S6 The factor analysis of Raman spectra temperature dependence of CS bovine trachea. Result of the one-step transition fit is shown by red lines.

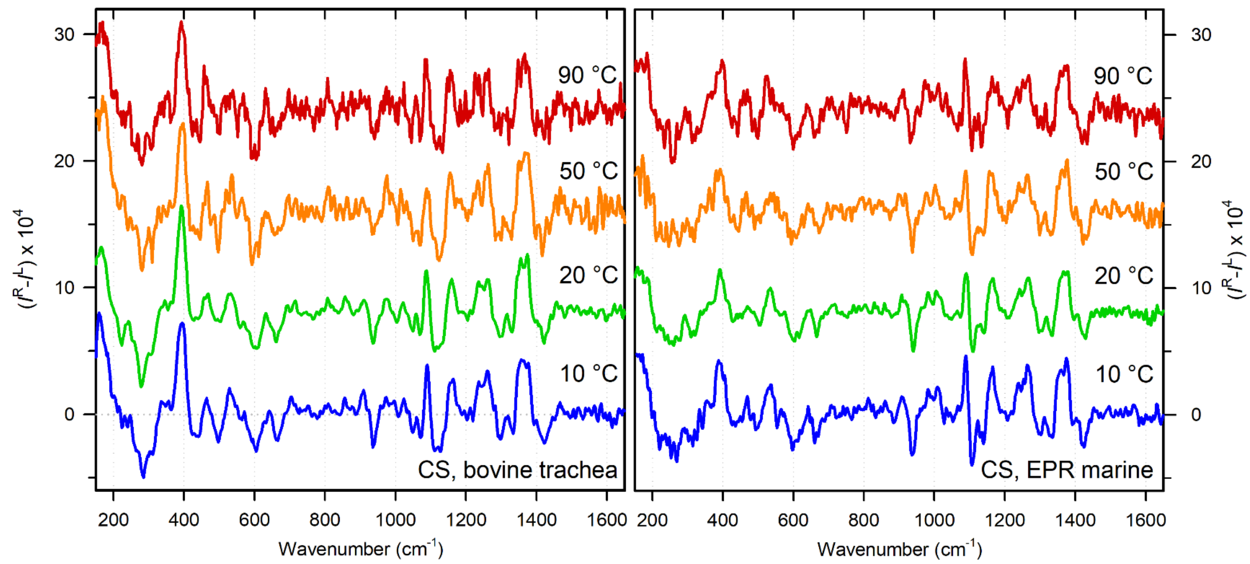

Fig. S7 ROA spectra of CS from bovine trachea (left) and CS EPR marine (right) at various temperatures. The spectra belong to the Raman spectra in Fig. S4 and Fig. 8 measured at each corresponding temperature. The same factor was used for normalization of both Raman and ROA spectra.