Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for:

Superalkali Nature of the Si_9M_5 (M=Li, Na, K) Zintl Clusters: A Theoretical Study on Electronic Structure and Dynamic Nonlinear Optical Properties

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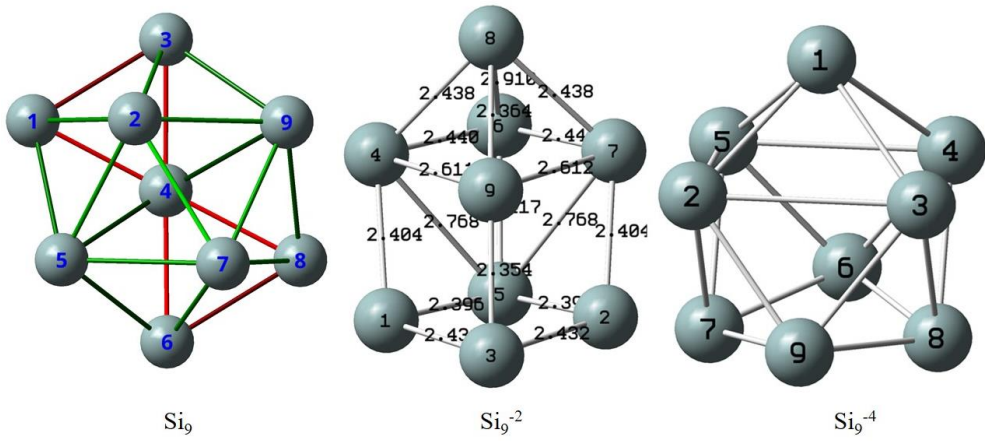

Figure S1. The optimized geometries of the Si_9 clusters at the ωb97xd/def2-qzvp level.

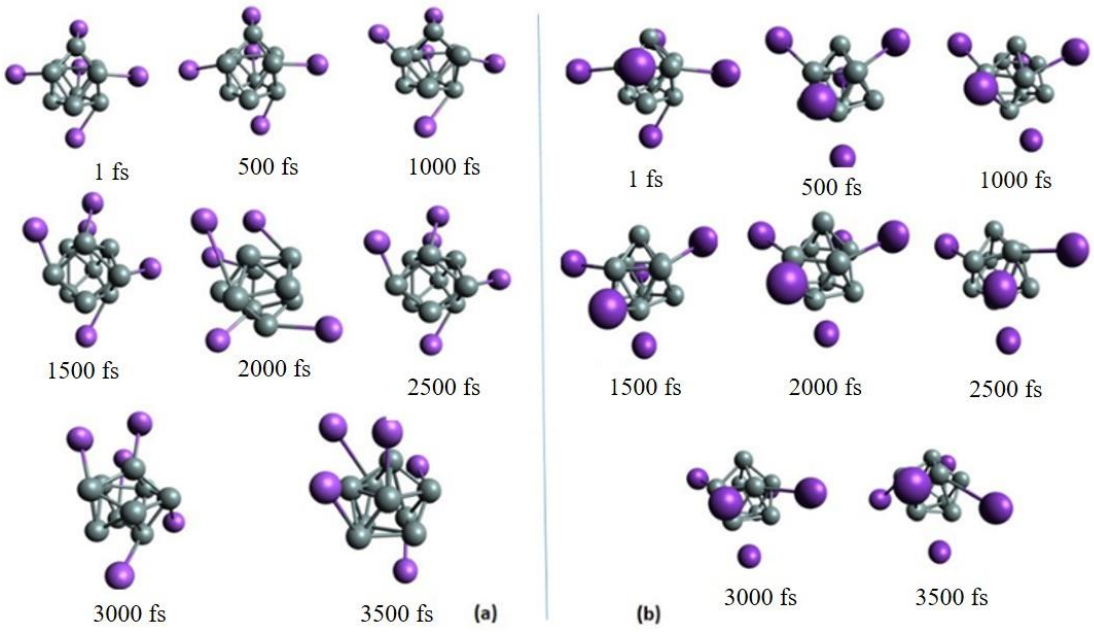

Figure S2. Snapshot of geometries at every 500 fs for (a) Si_9Na_5 and (b) Si_9K_5 during AIMD simulation at the B3LYP-D3/def2-SVP level.

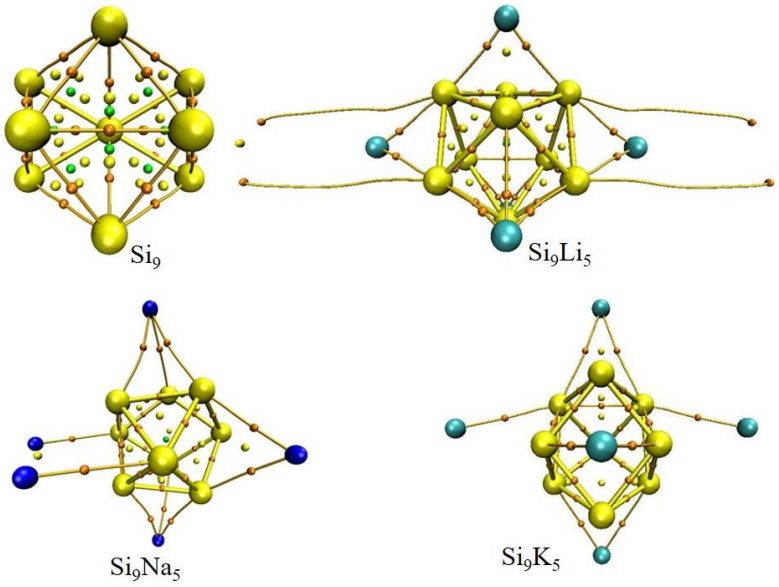

Figure S3. Quantum theory of atoms in molecules (QTAIM) analysis of the present clusters at the ωb97Xd/def2-qzvp level.

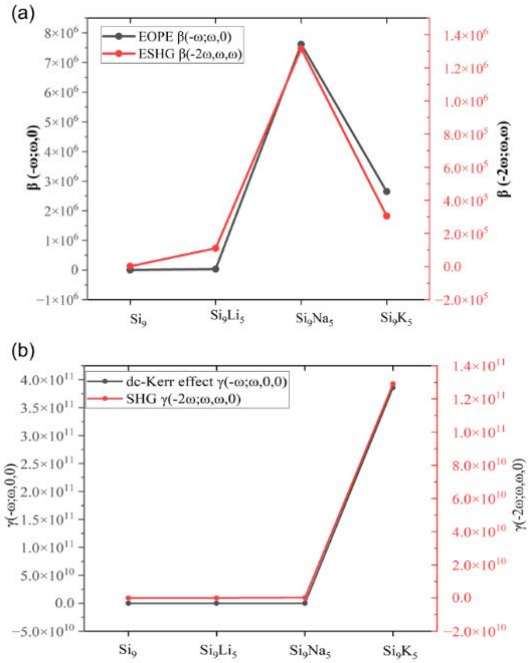

Figure S4. Frequency-dependent NLO response: (a) Plotted electro-optical-Pockel's effect EOPE β(-ω, ω,0) and ESHG β(-2ω,ω,ω) at the external frequency of 532 nm (b) dc-Kerr effect γ(-ω, ω,0,0) and second harmonic generation constant SHG γ(-2ω,ω,ω,0) at 1900 nm.

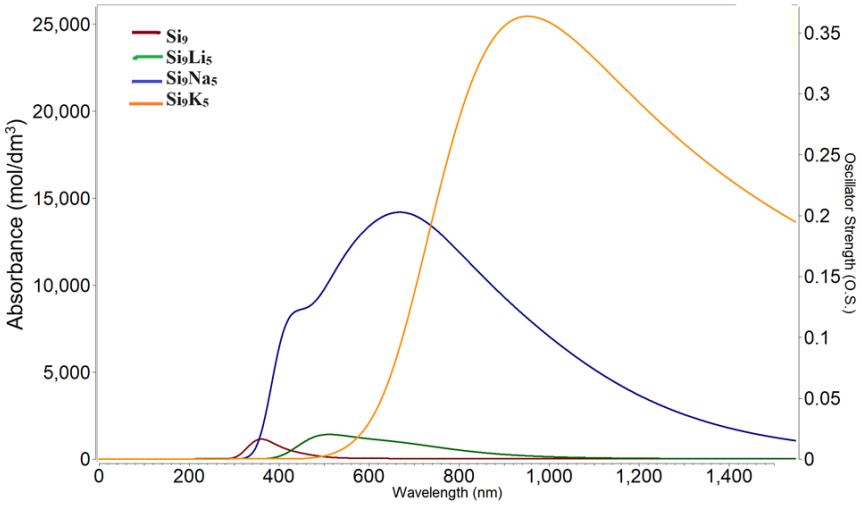

Figure S5. Absorption spectra of designed clusters at the ωb97xd/def2-qzvp level

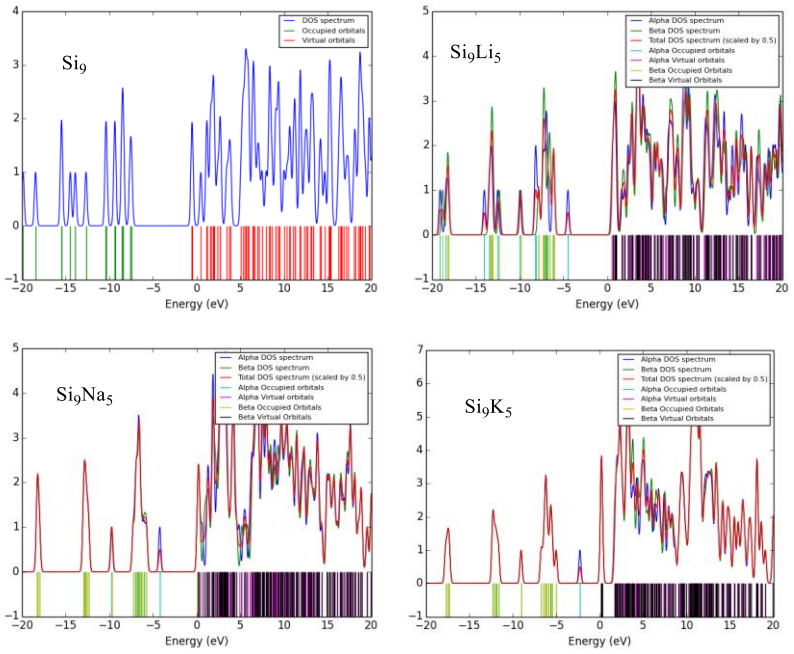

Figure S6. The total density of states (TDOS) spectra of Si_9 and Si_9M_5 at the ωb97xd/def2-qzvp level.

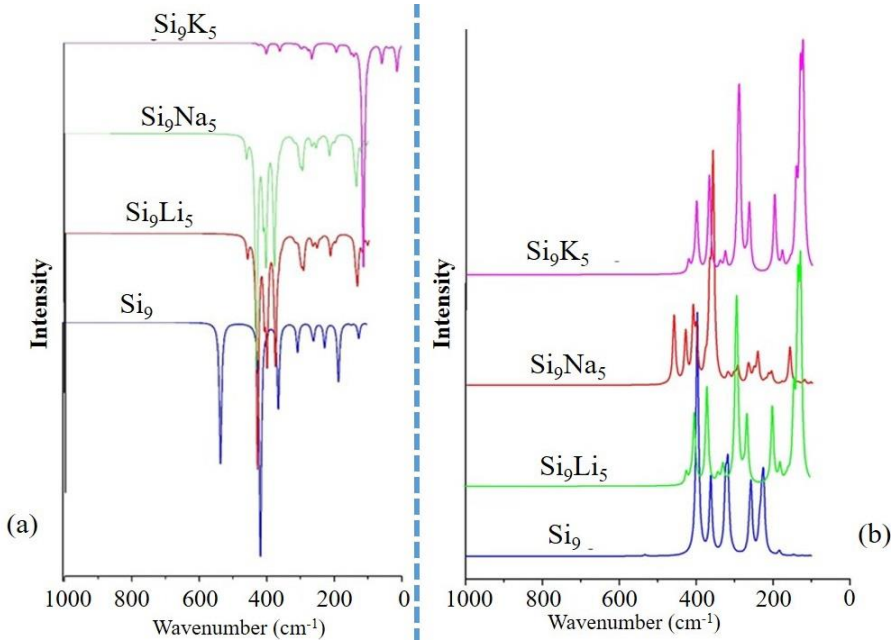

Figure S7. (a) FT-IR and (b) Raman spectrum of designed clusters at the ωb97xd/def2-qzvp level.

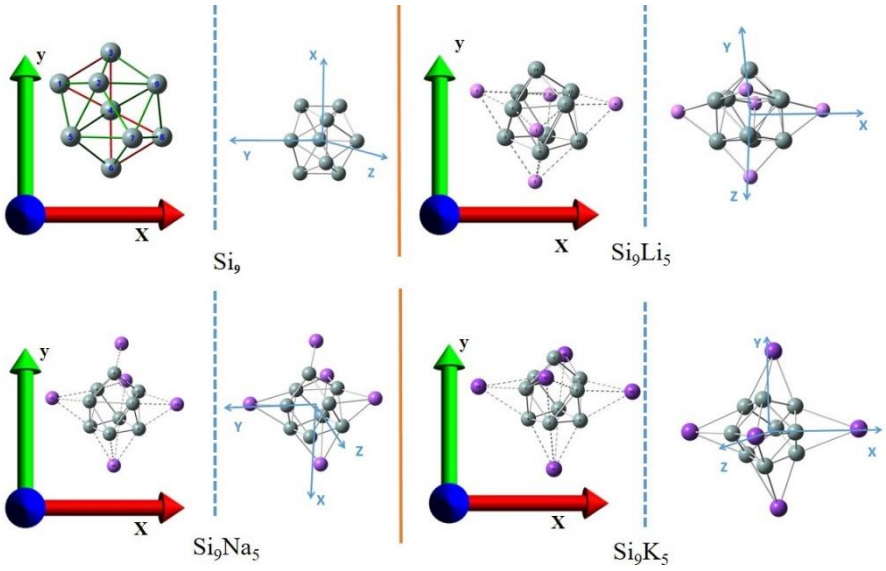

Figure S8. The optimized structures of the present clusters, in which the X-Y planes (with Z=0) are used to plot the electron localization function and 2D Localized orbital locator spectra for the present clusters.

Table S1. Optimized cartesian coordinates at the uwb97xd/ def2qzvp level.

Si_9

Si	2.04068700	1.18521600	-0.75198800
Si	1.29839400	0.00011300	1.34546700
Si	2.04071400	-1.18445800	-0.75310000
Si	-0.00004500	-0.00014500	-0.83051900
Si	-0.00083100	2.02685000	0.57446900
Si	-2.04066300	1.18445100	-0.75305200
Si	-1.29829100	0.00003600	1.34557100
Si	-2.04085500	-1.18525800	-0.75167000
Si	0.00089000	-2.02680400	0.57482200

Si_9Li_5

Li	3.71009300	-0.06767500	-0.26046500
Li	0.00025200	-1.73800000	2.73252700
Li	0.00004000	3.12415600	0.88833800
Li	-0.00016700	-2.42502600	-2.64597900
Li	-3.71010100	-0.06780700	-0.25999700
Si	1.69170800	-0.88144800	1.04612400
Si	1.26426100	-0.46704100	-1.41633000
Si	1.66859900	1.37702400	0.18716600
Si	0.00015900	0.72477000	1.95280600
Si	0.00003400	-2.15898800	-0.09902300
Si	-1.69148900	-0.88148700	1.04640900
Si	-1.26453800	-0.46705400	-1.41624300
Si	-1.66860000	1.37697900	0.18744700
Si	-0.00015900	1.62889200	-1.58573200

Si_9Na_5

Si	0.03916200	-0.00000900	1.96296400
Si	1.27410000	-1.64307900	0.62704100
Si	1.27419300	1.64300100	0.62704900
Si	-1.09134500	1.30964000	0.24152300
Si	-1.09142100	-1.30957600	0.24151700
Si	-1.33132900	0.00004200	-1.80819300
Si	0.66616300	-1.34334200	-1.72083700
Si	0.66624000	1.34330500	-1.72082800
Si	2.45665000	-0.00007300	-0.82474100
Na	3.17411700	-0.00008200	2.09046100
Na	-2.86647700	0.00010000	2.60083700
Na	0.02332200	3.97652200	-0.60688900
Na	-3.99710000	0.00009400	-0.45544500
Na	0.02306700	-3.97651900	-0.60686800

Si_9K_5

Si	-1.77026400	-0.00673800	1.27968100
Si	-1.44138100	1.27253800	-0.76195800
Si	-1.42879100	-1.28620700	-0.76007100
Si	-0.06494800	-1.77119200	1.18300700
Si	-0.08156700	1.77353800	1.18000200
Si	1.63804000	0.00932300	1.20155900
Si	1.25063800	1.25187500	-0.81833100
Si	1.26145200	-1.24013100	-0.81644600
Si	-0.14146300	-0.00148600	-2.38425200
K	4.71704100	0.01489600	-0.59864200
K	0.05771700	0.00404500	4.00575300
K	0.10126200	4.18125700	-1.12666300
K	-4.44319000	-0.02074400	-0.64503600
K	0.14064100	-4.18057400	-1.12197300

Table S2. Calculated bond lengths of the Si_9 and Si_9M_5 (M=Li, Na, K) clusters.

	Si-Si bonds	Distance (Å)	Si-M	Distance (Å)
Si_9	9-8=1-5=9-3=5-6	2.73	-	-
	4-8=4-6=4-1=4-3	2.52	-	-
	9-7=9-2=2-5=7-5=	2.76	-	-
	6-8=1-3	2.60	-	-
	2-7=2.82	2.71	-	-
Si_9Li_5	Si-Si(capped position (14,9,10)		Li(1,2,3,4,5)-Si	
	14-12=14-13=14-8=14-7	2.60	7-4, 12-4, 10-4=	2.77
	9-8=9-13=9-11=9-6	2.65	8-3=13-3=9-3	2.68
	10-7=10-12	2.68,	9-2=6-2=11-2=10-2	2.92
	10-6=10-11	2.54		
	7-8=13-12	2.70		
Si_9Na_5	Si-Si (capped position 2,3,6)		Na(14,12,13,10)-Si	
	2-7=2-5=2-9=2-1	2.46	14-5=14-2=14-7	3.02
	3-8=2.49, 3-4=	2.46	12-8=12-4=12-3	3.02
	3-9=3-1=2.47	2.47	10-3=10-2=2.91,	3.21
	6-4=6-5=2.47, 6-8=6-7	2.42	10-1=10-9	3.22
			11-4=11-6=11-5	3.01
Si_9K_5	Si-Si (capped position 5,4,9)		K(10,11,12,13,14)-Si	
	2-7=2-5=2-9=2-1	2.46	14-3=14-8=14-4	3.41
	3-8=2.49,	2.47	10-7=10-8	3.67
	3-4=2.46, 3-9=3-1	2.47	10-9=10-6	3.78
	6-4=6-5=2.47, 6-8=6-7	2.42	12-2=12-7=12-5	3.42
			13-2=12-3=2.85,13-1	3.65
			11-4=11-5	2.92,
			11-6=11-6	3.66

Table S3. NBO analysis based upon Fock matrix.

Cluster	Donor(i)	Type	Acceptor(j)	Type	$E_{(2)}$ [a] (kcal/mol)	E(*i*)-E(*j*) [b] (au)	F(*i*,*j*) [c] (au)
Si_9	Si3-Si4	σ	Si4-Si9	σ	46.39	0.09	0.166
	Si4-Si5	σ	Si4-Si6	σ	69.71	0.31	0.315
	Si4-Si6	σ	Si4-Si9	σ	80.41	0.02	0.091
	Si4-Si6	σ	Si4-Si5	σ*	29.82	0.29	0.212
	Si4-Si8	σ	Si4-Si6	σ*	26.95	0.45	0.262
	Si4-Si8	σ	Si3-Si4	σ*	28.07	0.31	0.213
	Si4-Si9	σ	Si4-Si8	σ	72.96	0.29	0.309
	Si4-Si5	σ *	Si4-Si8	σ*	28.39	0.02	0.007
Si_9Li_5	Si6-Si9	σ *	Si8-Si9	σ*	43.15	0.03	0.269
	Si6-Si9	σ *	Si9-Si13	σ *	36.30	0.03	0.245
	Si9-Si11	σ *	Si8-Si9	σ*	36.75	0.03	0.245
	Si9-Si11	σ *	Si9-Si13	σ*	44.86	0.03	0.269
Si_9Na_5	Si9-Si11	σ *	Si8-Si9	σ*	36.75	0.03	0.245
	Si9-Si11	σ *	Si9-Si13	σ*	44.86	0.03	0.269
	Si1-Si2	σ	Si5	LP* (2)	27.34	0.21	0.218
	Si3-Si4	σ	Si1-Si2	π*	18.20	0.06	0.086
	Si4-Si5	σ	Si1-Si2	π*	21.57	0.24	0.192
	Si7-Si9	π	Si1-Si2	π*	45.66	0.07	0.159
Si_9K_5	Si4-Si8	σ *	Si3-Si8	σ*	50.04	0.04	0.315
	Si3-Si8	σ	Si4-Si8	σ*	8.54	0.62	0.230
	Si3-Si8	σ	Si3-Si8	σ*	4.73	0.66	0.176

[a] $E_{(2)}$ means energy of hyper conjugative interactions. [b] Energy difference between donor and acceptor i and j NBO orbitals. [c] F(i,j) is the Fock matrix element between i and j NBO orbitals.

Table S4. Polarizability (α_o), and hyperpolarizability (β_o) parameters (in au) with different solvents using the ωb97xd/def2-qzvp method

	Acetone		Ethanol		Methanol		water	
	α_o	β_o	α_o	β_o	α_o	β_o	α_o	β_o
Si_9	4.9×10^2	2.4×10^2	4.9×10^2	2.4×10^2	5.0×10^2	2.3×10^2	5.1×10^2	2.1×10^2
Si_9Li_5	7.8×10^2	2.5×10^3	7.9×10^2	2.5×10^3	8.0×10^2	2.5×10^3	8.3×10^2	2.6×10^2
Si_9Na_5	1.0×10^3	8.2×10^4	1.0×10^2	7.8×10^4	1.0×10^3	7.3×10^4	2.6×10^3	6.1×10^4
Si_9K_5	2.4×10^3	2.9×10^6	2.5×10^3	8.1×10^6	2.7×10^3	3.9×10^6	3.0×10^2	5.5×10^6

Table S5. The calculated FT-IR and Raman spectrum values at the ωb97xd/def2-qzvp level.

Si_9			Si_9Li_5			Si_9Na_5			Si_9K_5			Assignments [a]
Wave number (cm^{-1})	IR Intensity	Raman activity	Wave number (cm^{-1})	IR intensity	Raman activity	Wave number (cm^{-1})	IR intensity	Raman activity	Wave number (cm^{-1})	IR intensity	Raman activity	
533	10	0.5										γ Si-Si (50)+ τ Si-Si-Si-Si(12)
			460	23.6	115.6							γ Si-Li (48)
			431	205	2.61							γ Si-Li (38)
			430	65.7	82.2							γ Si-Li (40)
									423	5.4	83.0	γ Si-Si (41)+ β SiSiSi(12)+ τ K-Si-Si-Si(12)
						421	2.8	34.5				γ Si-Si (41)+ β SiSiSi(12)
415	17	0										γ Si-Si (49)+ β SiSiSi(17)
			410	74.2	113.9				410	3.3	72.6	γ Si-Li/K (22)+ β Li/KSiSi(10)
			402	131.8	75.9							γ Si-Si (37)
						401	1.9	201.8				γ Si-Si (46)
									400	5.3	226.0	γ Si-Si (52)
397	17.9	106.5										γ Si-Si (50)+ τ Si-Si-Si-Si(10)
			379	53.3	23.8							γ Si-Li (13)+ β LiSiSi(13)
			377	103.5	4.3							γ Si-Li (25)+ γ Si-Si (12)
						368	6.4	262.6				γ Si-Si (34)
			367	16.4	141.6							γ Si-Si (27)+ τ Si-Si-Si-Si(13)
362	4.5	28.3										γ Si-Si (28)+ β SiSiSi(12)
									361	4.5	784.7	γ Si-Si (16)+ τ Si-Si-Si-Si(43)
			359	5.9	369.5							γ Si-Si (27)+ τ Si-Si-Si-Si(12)
						326	7.1	54.3				γ Si-Si (16)+ γ Si-Na (12) + τ Si-Si-Si-Si(24)
323	0	28.12										γ Si-Si (28)+ β SiSiSi(31)
317	0	34.9										γ Si-Si (27)+ β SiSiSi(14))+ τ Si-Si-Si-Si(12)
									309	1.0	50.4	γ Si-Si (32)+ β SiSiSi(12))+ τ K-Si-Si-Si(11)
									295	7.4	295.3	β KSiSi(42))+ τ K-Si-Si-K(19)
						293	4.5	218.7				β SiSiSi(24))+ τ Si-Si-Si-Si(12)
						290	6.1	402.8				β SiSiSi(50))+ τ Si-Si-Si-Si(12)
									286	6.5	221.8	β KSiSi(24))+ τ Si-Si-Si-Si(27)
									277	14.4	289.1	β SiSiSi(38))+ τ Si-Si-Si-Si(13)
						275	13.9	2.8				β SiSiSi(22))+ τ Si-Si-Si-Si(16)
									266	4.0	4.0	β SiSiSi(18) + τ Si-Si-Si-Si(35)
						264	0	189.1				β SiSiSi(15) + τ Si-Si-Si-Si(10)
									260	6.0	188.7	γ Si-Si (11)+ β SiSiSi(18) + τ Si-Si-Si-Si(24)
257	1.2	28.6										γ Si-Si (27)+ β SiSiSi(12) + τ Si-Si-Si-Si(12)
			242	2.8	51.9							β SiSiSi(11) + τ Si-Si-Si-Si(10)
224	1.9	29.1										β SiSiSi(47)
						198	42.2	218.7				γ Si-Na (31)
						197	80.1	4.0				γ Si-Na (52)
183	4.6	2.1										γ Si-Si (31)+ β SiSiSi(13) + τ Si-Si-Si-Si(11)
						163	33.5	6.5				β SiSiSi(11)
			159	0.6	63.9							β SiSiSi(10)
						157	20.5	15.7				γ Si-Na (53)
						142	35.5	223.9				β NaSiSi(16) + τ Si-Si-Si-Si(33)
			134	51.5	134.2							βLiSiSi(15) +τ Li-Si-Si-Si(14) +τ Li-Si-Li-Si(14)
						131	0.4	471.0				γ Si-Na (49)
						124	5.6	542.2				γ Si-Na (18)
									112	607	8.7	τ K-Si-K-Si(19)

[a] γ is stretching, β is bending, and τ is torsion.