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

Supplementary information for Covalent functionalization of germanene employing computational simulations

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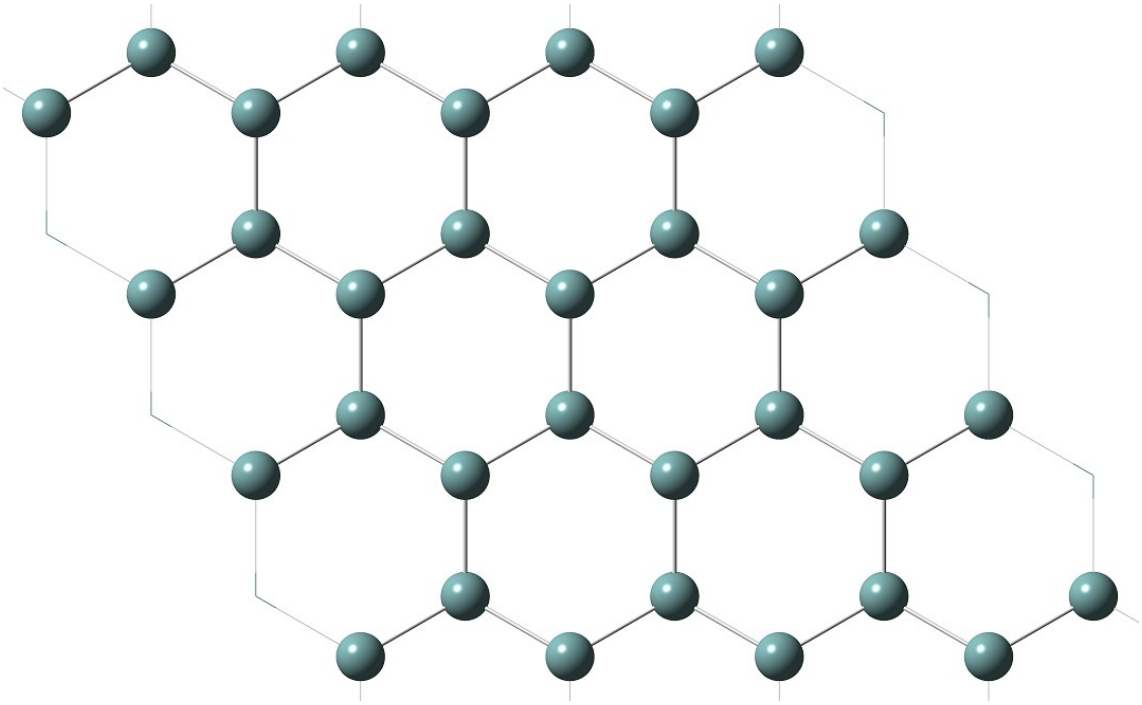

Figure S1. Optimized structure for germanene 4×4 unit cell employed in this study for the periodic boundary conditions calculations, at the M06-L/6-311G* level of theory.

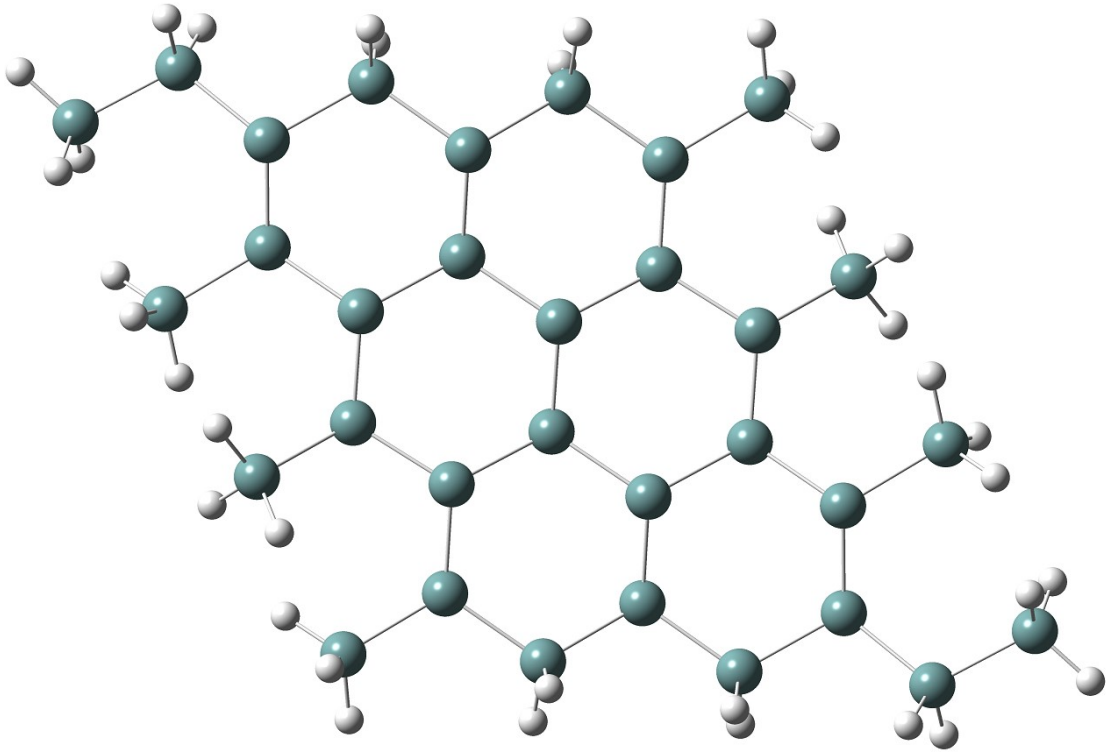

Figure S2. Optimized structure for germanene flake used to compute thermodynamic corrections, at the M06-L/6-311G* level of theory.

Table S1. Ge-Ge bond distances determined at the M06-L/6-311G* level of theory.[a,b]

H	2.48
O[c]	3.13
OH	2.49
S	2.49
Se	2.50
F	2.48
Cl	2.49
Br	2.49
CH_3	2.49
CF_3	2.48
NH[c]	3.09
NH_2	2.50
SH	2.49
C_6H_5	2.49
C_6H_4	2.51
Azomethine-I	2.49
CCl_2	2.56
CBr_2	2.56

a) The Ge-Ge bond distance in monolayer germanene is 2.42 Å.
b) For H, OH, F, Cl, Br, CH_3, CF_3, NH_2 and C_6H_5, The distance reported corresponds to the average of the three Ge-Ge bond distances that the reacting Ge atom forms with its three neighbors. In the case of O, S, Se, C_6H_4, azomethine, CCl_2 and CBr_2 the Ge-Ge distance reported is the one between the Ge atoms that react with the functional groups, as they are bonded to two Ge atoms.
c) Only for the addition of O and NH the Ge-Ge bond is broken.

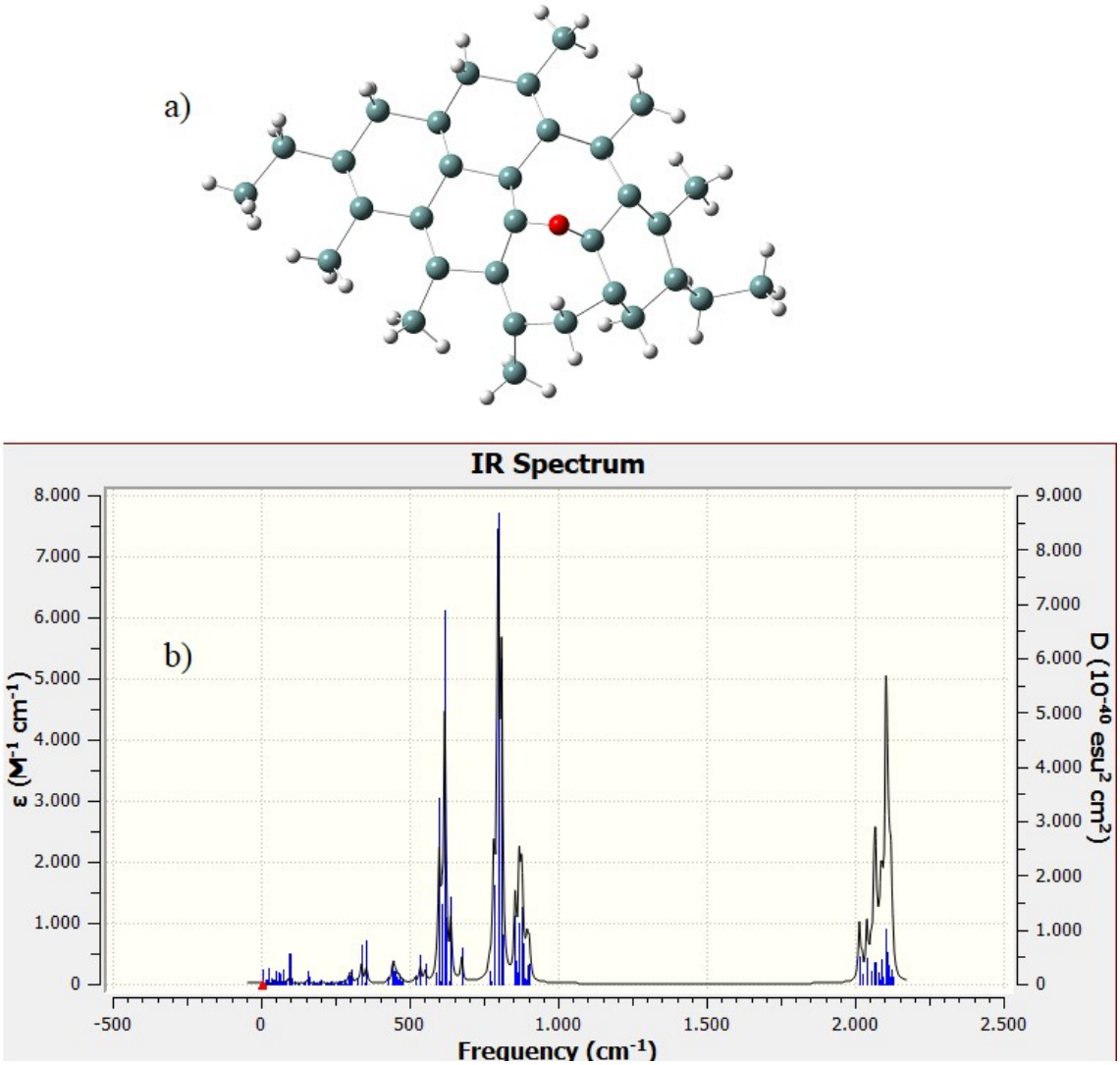

Figure S3. a) Optimized structure for germanene flake functionalized with an oxygen atom used to compute thermodynamic corrections, at the M06-L/6-311G* level of theory, b) Vibrational analysis.

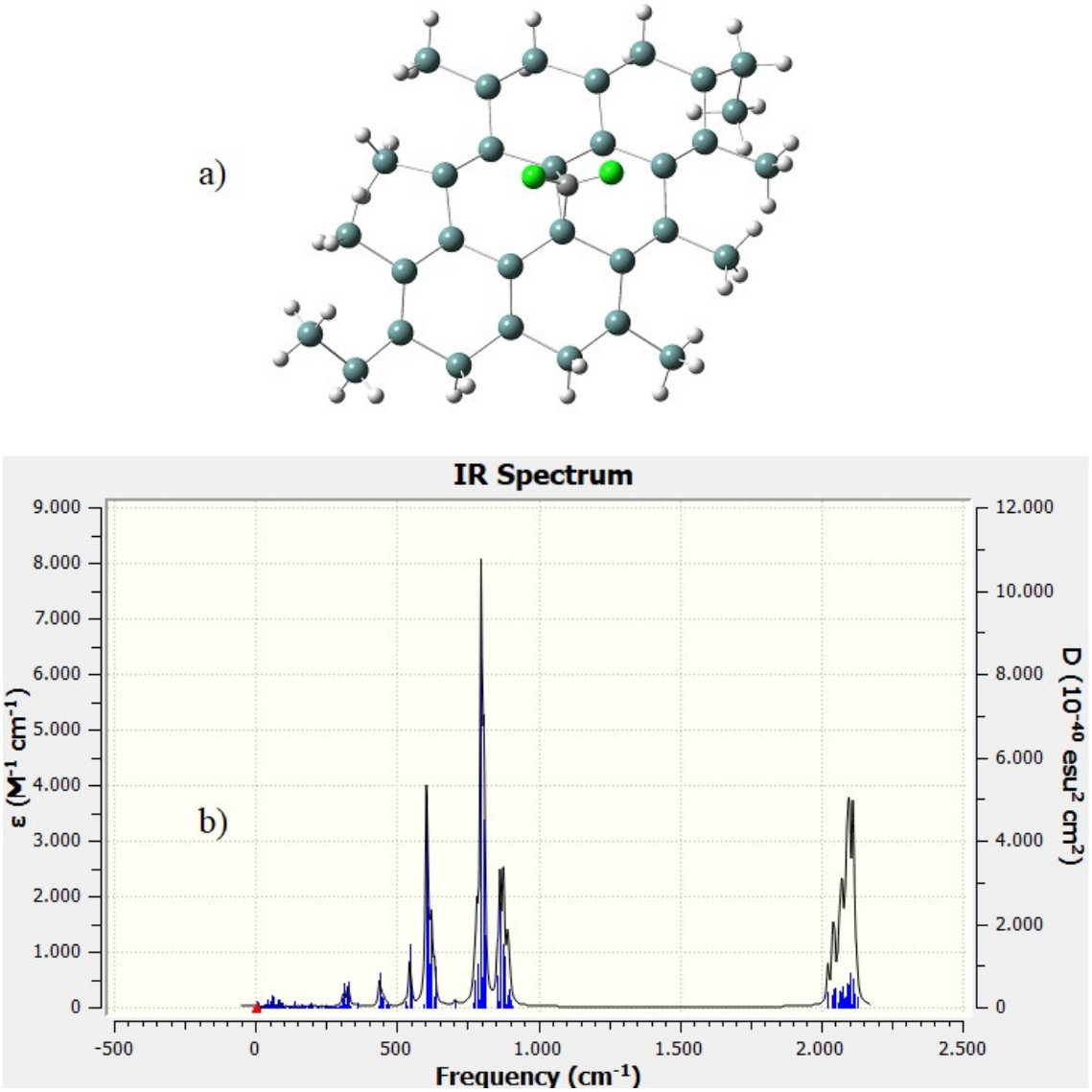

Figure S4. a) Optimized structure for germanene flake functionalized with an oxygen atom used to compute thermodynamic corrections, at the M06-L/6-311G* level of theory, b) Vibrational analysis.

Anex I: Vibrational frequency analysis of O-05% functionalized germanene (six atoms unit cell, periodic calculation).

	1			2			3		
	A			A			A		
Frequencies --	36.0372			39.5823			104.2246		
Red. masses --	73.8660			58.2153			50.5330		
Frc consts --	0.0565			0.0537			0.3234		
IR Inten	--5430675.1951			331172.3340			1773508.4142		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 32	-0.50	0.00	-0.01	0.01	0.05	-0.42	0.00	0.09	0.21
2 32	0.50	0.00	0.01	0.00	0.03	0.42	0.00	-0.04	0.50
3 32	0.50	0.00	0.01	0.00	0.03	0.43	0.00	0.04	-0.49
4 32	-0.50	0.00	-0.01	0.01	0.04	-0.43	-0.01	-0.09	-0.21
5 8	-0.02	0.00	0.00	-0.01	-0.37	0.00	0.05	-0.05	0.44
6 8	-0.02	-0.01	0.00	0.00	-0.37	0.00	0.04	0.05	-0.44
7 -2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8 -2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	4			5			6		
	A			A			A		
Frequencies --	125.7300			130.1549			161.9294		
Red. masses --	17.6890			60.7459			18.0967		
Frc consts --	0.1648			0.6063			0.2796		
IR Inten	--**********			1774456.8940			**********		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 32	0.08	0.00	0.06	-0.03	0.01	0.56	0.10	0.00	0.00
2 32	0.07	-0.01	-0.02	-0.03	-0.06	-0.28	0.09	0.00	0.00
3 32	0.07	0.01	0.01	-0.02	0.06	0.27	-0.10	0.00	0.00
4 32	0.08	0.00	-0.05	-0.02	-0.01	-0.55	-0.10	0.00	0.00
5 8	-0.69	0.02	0.03	0.20	0.19	0.18	0.70	0.00	0.00
6 8	-0.70	-0.01	-0.02	0.23	-0.18	-0.18	-0.69	0.00	0.00
7 -2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8 -2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	7			8			9		
	A			A			A		
Frequencies --	187.2892			239.2073			260.8141		
Red. masses --	56.3748			59.2371			62.2960		
Frc consts --	1.1651			1.9971			2.4967		
IR Inten	--6226452.6265			1031397.0583			2727601.1652		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 32	0.00	0.41	0.00	0.00	-0.43	0.03	0.00	0.44	-0.14
2 32	0.00	0.42	-0.03	0.00	0.42	0.04	0.00	-0.43	-0.12
3 32	0.00	-0.42	0.03	0.00	0.43	0.05	0.00	0.42	0.12
4 32	0.00	-0.41	0.00	0.00	-0.44	0.04	0.00	-0.43	0.13
5 8	0.00	0.39	-0.03	-0.01	0.01	-0.35	0.00	-0.01	0.32
6 8	0.00	-0.39	0.03	0.00	0.01	-0.36	0.00	0.01	-0.31
7 -2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8 -2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	10			11			12		

	A	A	A
Frequencies --	296.4978	304.6538	471.0290
Red. masses --	70.2724	49.8006	18.4851
Frc consts --	3.6398	2.7233	2.4164
IR Inten --	1037098.9475	5801701.0855	**********

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.60	0.00	0.00	0.24	0.00	0.00	0.00	0.08	0.08
2	32	-0.33	0.00	0.00	0.49	0.00	0.00	0.00	0.07	-0.07
3	32	0.33	0.00	0.00	-0.49	0.00	0.00	0.00	0.07	-0.07
4	32	-0.60	0.00	0.00	-0.24	0.00	0.00	0.00	0.08	0.08
5	8	-0.18	0.00	0.00	-0.46	0.00	0.00	0.00	-0.69	-0.06
6	8	0.18	0.00	0.00	0.46	0.00	0.00	0.00	-0.69	-0.06
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	13	14	15
	A	A	A
Frequencies --	528.2326	635.2158	643.8401
Red. masses --	17.4459	18.8706	18.3920
Frc consts --	2.8681	4.4862	4.4920
IR Inten --	**********	**********	**********

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.00	-0.08	-0.05	0.00	-0.07	-0.07	0.00	0.06	0.07
2	32	0.00	-0.06	0.03	0.00	0.09	-0.08	0.00	-0.08	0.08
3	32	0.00	0.06	-0.03	0.00	-0.09	0.09	0.00	-0.07	0.08
4	32	0.00	0.08	0.05	0.00	0.07	0.07	0.00	0.06	0.07
5	8	0.00	0.69	0.09	0.00	-0.09	0.66	0.00	0.06	-0.71
6	8	0.00	-0.69	-0.09	0.00	0.10	-0.70	0.00	0.06	-0.67
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Anex II: Vibrational frequency analysis of S-05% functionalized germanene (six atoms unit cell, periodic calculation).

	1	2	3
	A	A	A
Frequencies --	23.2842	39.9809	59.1745
Red. masses --	57.6274	73.9192	69.4715
Frc consts --	0.0184	0.0696	0.1433
IR Inten	--1363973.2706	**********	**********

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.00	0.09	-0.37	-0.50	0.00	-0.01	-0.02	-0.13	0.46
2	32	0.00	0.09	0.37	0.50	0.00	0.00	-0.01	-0.13	-0.46
3	32	0.00	0.10	0.39	0.50	0.00	0.00	-0.01	0.13	0.44
4	32	0.00	0.10	-0.38	-0.50	0.00	0.00	-0.02	0.13	-0.45
5	16	0.00	-0.44	0.00	0.00	0.00	0.00	0.08	0.23	0.00
6	16	0.00	-0.44	0.00	0.00	0.00	0.00	0.05	-0.21	0.00
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	4	5	6
	A	A	A
Frequencies --	67.2287	96.5268	119.3139
Red. masses --	35.6382	32.4933	58.6800
Frc consts --	0.0949	0.1784	0.4922
IR Inten	--8149024.6467	2603618.2658	182432.5322

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.15	-0.01	0.02	0.06	0.00	-0.01	0.00	-0.01	0.40
2	32	0.14	-0.01	-0.02	0.06	0.00	0.00	0.00	0.01	0.40
3	32	0.14	0.00	0.02	-0.05	0.00	0.00	0.00	-0.01	-0.40
4	32	0.15	0.01	-0.02	-0.05	0.00	0.01	0.00	0.01	-0.40
5	16	-0.68	0.01	0.00	0.70	0.00	0.00	0.01	0.00	0.43
6	16	-0.67	-0.01	0.00	-0.71	0.00	0.00	0.00	0.00	-0.43
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	7	8	9
	A	A	A
Frequencies --	176.3213	260.9772	277.7519
Red. masses --	48.9668	67.0014	41.1600
Frc consts --	0.8969	2.6887	1.8709
IR Inten	--1092348.7997	919223.7946	6829029.6654

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.00	0.32	0.03	0.00	-0.45	0.06	0.00	0.14	0.19
2	32	0.00	0.32	-0.03	0.00	0.45	0.06	0.00	0.13	-0.19
3	32	0.00	-0.32	0.03	0.00	0.45	0.06	0.00	0.13	-0.19
4	32	0.00	-0.32	-0.03	0.00	-0.45	0.06	0.00	0.14	0.19
5	16	0.00	0.55	0.00	0.00	0.00	-0.29	0.00	-0.62	0.00
6	16	0.00	-0.55	0.00	0.00	0.00	-0.29	0.00	-0.62	0.00
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	10	11	12
	A	A	A
Frequencies --	291.6116	297.6666	303.7569
Red. masses --	71.2950	62.1181	73.9207
Frc consts --	3.5721	3.2429	4.0185
IR Inten --	**********	2586975.0944	3632519.6884

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.49	0.00	0.00	0.00	0.41	-0.08	0.50	0.00	0.00
2	32	0.48	0.00	0.00	0.00	-0.42	-0.08	-0.50	0.00	0.00
3	32	-0.48	0.00	0.00	0.00	0.42	0.08	0.50	0.00	0.00
4	32	-0.49	0.00	0.00	0.00	-0.41	0.08	-0.50	0.00	0.00
5	16	-0.18	0.00	0.00	0.00	0.01	0.38	0.00	0.00	0.00
6	16	0.18	0.00	0.00	0.00	-0.01	-0.37	0.00	0.00	0.00
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	13	14	15
	A	A	A
Frequencies --	312.4867	446.4558	449.0734
Red. masses --	42.4075	39.6903	37.4196
Frc consts --	2.4398	4.6611	4.4462
IR Inten --	**********	4284330.1700	2518535.1178

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.00	-0.22	-0.13	0.00	-0.15	-0.15	0.00	0.11	0.14
2	32	0.00	-0.21	0.13	0.00	0.15	-0.15	0.00	-0.11	0.15
3	32	0.00	0.21	-0.13	0.00	-0.16	0.15	0.00	-0.11	0.14
4	32	0.00	0.22	0.13	0.00	0.15	0.15	0.00	0.11	0.14
5	16	0.00	0.61	0.00	0.00	0.00	0.63	0.00	0.00	-0.67
6	16	0.00	-0.61	0.00	0.00	0.00	-0.65	0.00	0.00	-0.65
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Anex III: Vibrational frequency analysis of Se-05% functionalized germanene (six atoms unit cell, periodic calculation).

	1	2	3						
	A	A	A						
Frequencies --	20.4774	30.0769	37.3906						
Red. masses --	75.6135	77.7051	73.9212						
Frc consts --	0.0187	0.0414	0.0609						
IR Inten	--**********	944814.9264	7788236.3694						
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.00	0.20	-0.37	0.30	0.00	0.00	-0.50	0.00	0.00
2	32	0.00	0.20	0.37	0.30	0.00	0.00	0.50	0.00	0.00
3	32	0.00	0.20	0.37	0.30	0.00	0.00	0.50	0.00	0.00
4	32	0.00	0.20	-0.37	0.30	0.00	0.00	-0.50	0.00	0.00
5	34	0.00	-0.38	0.00	-0.56	0.00	0.00	0.00	0.00	0.00
6	34	0.00	-0.38	0.00	-0.56	0.00	0.00	0.00	0.00	0.00
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	4	5	6						
	A	A	A						
Frequencies --	49.9973	74.7933	102.0460						
Red. masses --	79.8680	75.2762	76.4196						
Frc consts --	0.1176	0.2481	0.4689						
IR Inten	--1362485.0046	765017.2040	1103612.7140						
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.04	0.00	0.00	0.00	-0.12	0.43	0.00	-0.01	0.38
2	32	0.04	0.00	0.00	0.00	-0.12	-0.42	0.00	0.01	0.38
3	32	-0.04	0.00	0.01	0.00	0.12	0.42	0.00	-0.01	-0.38
4	32	-0.04	0.00	0.00	0.00	0.12	-0.43	0.00	0.01	-0.38
5	34	0.70	0.00	0.00	-0.01	0.34	0.00	0.00	0.00	0.46
6	34	-0.70	0.00	0.00	0.00	-0.34	0.00	0.00	0.00	-0.46
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	7	8	9						
	A	A	A						
Frequencies --	129.8185	203.9743	235.4550						
Red. masses --	77.4969	75.9191	75.4840						
Frc consts --	0.7695	1.8610	2.4656						
IR Inten	-- 857182.6622	6332106.0877	46313.5246						
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.00	0.28	-0.16	0.00	0.22	0.34	0.00	-0.38	0.19
2	32	0.00	0.28	0.16	0.00	0.22	-0.34	0.00	0.38	0.20
3	32	0.00	-0.28	-0.16	0.00	0.22	-0.34	0.00	0.38	0.20
4	32	0.00	-0.28	0.16	0.00	0.22	0.34	0.00	-0.38	0.19
5	34	0.00	0.55	0.00	0.00	-0.41	0.00	0.00	0.00	-0.36
6	34	0.00	-0.55	0.00	0.00	-0.41	0.00	0.00	0.00	-0.36
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	10	11	12
	A	A	A
Frequencies --	248.5564	252.7358	280.5887
Red. masses --	74.7355	76.1551	73.9625
Frc consts --	2.7204	2.8660	3.4309
IR Inten	--4385282.2027	4229539.3496	**********

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.00	0.40	0.23	0.00	0.30	-0.27	0.50	0.00	0.00
2	32	0.00	0.41	-0.22	0.00	-0.28	-0.28	0.50	0.00	0.00
3	32	0.00	-0.41	0.22	0.00	0.28	0.28	-0.50	0.00	0.00
4	32	0.00	-0.40	-0.23	0.00	-0.30	0.27	-0.50	0.00	0.00
5	34	0.00	-0.26	-0.01	0.00	-0.01	0.43	-0.06	0.00	0.00
6	34	0.00	0.26	0.01	0.00	0.01	-0.43	0.06	0.00	0.00
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	13	14	15
	A	A	A
Frequencies --	296.2365	317.1505	344.6712
Red. masses --	73.9212	76.0500	74.8934
Frc consts --	3.8220	4.5069	5.2421
IR Inten	--5859394.0220	401742.1057	2060644.2874

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	32	0.50	0.00	0.00	0.00	0.33	0.23	0.00	0.41	0.19
2	32	-0.50	0.00	0.00	0.00	-0.33	0.23	0.00	-0.42	0.19
3	32	0.50	0.00	0.00	0.00	-0.33	0.23	0.00	0.42	-0.19
4	32	-0.50	0.00	0.00	0.00	0.33	0.23	0.00	-0.41	-0.19
5	34	0.00	0.00	0.00	0.00	0.00	-0.42	0.00	0.00	-0.29
6	34	0.00	0.00	0.00	0.00	0.00	-0.42	0.00	0.00	0.28
7	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00