Table S1. Theoretical harmonic vibrational wavenumbers (cm^{-1}) for SnX_2 (X = H, F, Cl, Br, and I) species with C_{2v} symmetry at the B3LYP, BLYP and BHLYP functionals.

Species	Functionals	Frequencies (cm^{-1})			
		Neutral	**Anion**	**Cation**	**Triplet**
SnH_2	B3LYP	813, 1674, 1684	753, 1420, 1436	709, 1776, 1849	693, 1774, 1848
	BLYP	788, 1618, 1627	725, 1365, 1377	690, 1701, 1782	673, 1701, 1786
	BHLYP	850, 1741, 1755	792, 1482, 1503	736, 1865, 1928	721, 1858, 1920
	Experimental	1682 [1]	1506 [1]		
SnF_2	B3LYP	188, 525, 547	158, 401, 429	146, 560, 583	130, 506, 530
	BLYP	178, 501, 521	148, 378, 407	137, 528, 553	120, 471, 495
	BHLYP	201, 550, 574	170, 423, 453	159, 599, 620	141, 546, 570
	Experimental	201, 584, 605 [2]			
SnCl_2	B3LYP	108, 307, 323	79, 223, 245	85, 305, 330	73, 274, 308
	BLYP	102, 294, 309	75, 212, 233	78, 283, 309	67, 253, 285
	BHLYP	116, 320, 337	84, 231, 254	93, 326, 350	80, 296, 331
SnBr_2	B3LYP	72, 219, 228	51, 158, 172	72, 219, 228	50, 183, 223
	BLYP	68, 210, 217	49, 150, 163	55, 187, 223	46, 167, 207
	BHLYP	77, 228, 238	54, 164, 179	65, 221, 257	55, 198, 241
SnI_2	B3LYP	53, 169, 170	36, 122, 129	41, 136, 152	33, 121, 158
	BLYP	50, 163, 163	34, 117, 123	40, 121, 139	30, 108, 146
	BHLYP	57, 175, 176	38, 125, 133	44, 146, 159	35, 129, 166

Table S2. Vertical electron affinities (EA_{vert}) in eV.

	BHLYP	BLYP	B3LYP
SnH_2	0.78	0.73	0.90
SnF_2	0.87	0.77	0.96
SnCl_2	1.67	1.47	1.70
SnBr_2	1.72	1.52	1.75
SnI_2	2.20	1.86	2.15
SnHF	0.85	0.77	0.95
SnHCl	1.27	1.15	1.34
SnHBr	1.31	1.18	1.38
SnHI	1.56	1.37	1.59
SnFCl	1.30	1.15	1.36
SnFBr	1.34	1.18	1.39
SnFI	1.60	1.38	1.62
SnClBr	1.69	1.49	1.72
SnClI	1.95	1.67	1.93
SnBrI	1.96	1.69	1.95
H**Sn**CH_3	0.63	0.60	0.75
F**Sn**CH_3	0.69	0.63	0.79
Cl**Sn**CH_3	1.07	0.96	1.14
Br**Sn**CH_3	1.11	1.01	1.19
I**Sn**CH_3	1.36	1.19	1.40
H**Sn**SiH_3	1.29	1.26	1.42
F**Sn**SiH_3	1.36	1.30	1.47
Cl**Sn**SiH_3	1.67	1.56	1.75
Br**Sn**SiH_3	1.69	1.58	1.77
I**Sn**SiH_3	1.92	1.74	1.96
H**Sn**GeH_3	1.32	1.31	1.45
F**Sn**GeH_3	1.38	1.34	1.50
Cl**Sn**GeH_3	1.73	1.59	1.77
Br**Sn**GeH_3	1.71	1.61	1.79
I**Sn**GeH_3	1.93	1.77	1.98
H**Sn**SnH_3	1.43	1.38	1.54
F**Sn**SnH_3	1.50	1.42	1.60
Cl**Sn**SnH_3	1.81	1.68	1.88
Br**Sn**SnH_3	1.82	1.69	1.89
I**Sn**SnH_3	2.04	1.85	2.07
Sn$(CH_3)_2$	0.46	0.46	0.60
Sn$(SiH_3)_2$	1.64	1.58	1.74
Sn$(GeH_3)_2$	1.66	1.65	1.79
Sn$(SnH_3)_2$	1.89	1.83	2.00
CH_3**Sn**SiH_3	1.10	1.08	1.23
CH_3**Sn**GeH_3	1.13	1.13	1.27
CH_3**Sn**SnH_3	1.25	1.21	1.36
SiH_3**Sn**GeH_3	1.64	1.62	1.77
SiH_3**Sn**SnH_3	1.77	1.72	1.88
GeH_3**Sn**SnH_3	1.78	1.75	1.90

Table S3. Vertical detachment energies (VDE) in eV.

	BHLYP	BLYP	B3LYP
SnH_2	0.85	0.80	0.97
SnF_2	1.27	1.16	1.35
SnCl_2	2.19	1.94	2.19
SnBr_2	2.24	1.98	2.23
SnI_2	2.68	2.29	2.59
SnHF	1.09	1.01	1.19
SnHCl	1.62	1.47	1.67
SnHBr	1.67	1.51	1.72
SnHI	1.94	1.71	1.94
SnFCl	1.78	1.59	1.82
SnFBr	1.83	1.64	1.86
SnFI	2.12	1.85	2.11
SnClBr	2.22	1.96	2.21
SnClI	2.45	2.14	2.40
SnBrI	2.46	2.03	2.43
H**Sn**CH_3	0.73	0.71	0.86
F**Sn**CH_3	0.92	0.86	1.02
Cl**Sn**CH_3	1.41	1.28	1.47
Br**Sn**CH_3	1.47	1.34	1.53
I**Sn**CH_3	1.74	1.53	1.75
H**Sn**SiH_3	1.49	1.46	1.61
F**Sn**SiH_3	1.67	1.59	1.77
Cl**Sn**SiH_3	2.06	1.91	2.12
Br**Sn**SiH_3	2.09	1.94	2.14
I**Sn**SiH_3	2.30	2.09	2.32
H**Sn**GeH_3	1.52	1.52	1.66
F**Sn**GeH_3	1.70	1.65	1.81
Cl**Sn**GeH_3	2.14	1.95	2.14
Br**Sn**GeH_3	2.10	1.97	2.16
I**Sn**GeH_3	2.31	2.12	2.34
H**Sn**SnH_3	1.73	1.66	1.83
F**Sn**SnH_3	1.91	1.81	1.99
Cl**Sn**SnH_3	2.27	2.10	2.31
Br**Sn**SnH_3	2.29	2.11	2.33
I**Sn**SnH_3	2.50	2.26	2.50
Sn$(CH_3)_2$	0.59	0.59	0.72
Sn$(SiH_3)_2$	1.93	1.88	2.04
Sn$(GeH_3)_2$	1.96	1.96	2.10
Sn$(SnH_3)_2$	2.34	2.24	2.43
CH_3**Sn**SiH_3	1.31	1.29	1.43
CH_3**Sn**GeH_3	1.34	1.35	1.48
CH_3**Sn**SnH_3	1.56	1.51	1.66
SiH_3**Sn**GeH_3	1.94	1.92	2.07
SiH_3**Sn**SnH_3	2.14	2.07	2.24
GeH_3**Sn**SnH_3	2.16	2.11	2.27

Table S4. Summary of reported experimental values for the geometries, electron affinities and ionization energies in eV.

Species	Structural parameters	EA	IE (eV)
SnF_2			11.10 [10]
			11.48 [10]
			11.5 ± 0.2 [8]
			10.5 ± 0.3 [11]
SnCl_2	r(Sn–Cl) = 2.338 Å; θ = 97.7 ± 0.8° [3]	1.04 [9]	10.0 [12]
	r(Sn–Cl) = 2.345 Å; θ = 98.5° [4]		10.31 [12]
	r(Sn–Cl) = 2.335 Å; θ = 99.1° [5]		10.37 ± 0.05 [13]
	r(Sn–Cl) = 2.347 Å; θ = 99.0° [6]		10.31 ± 0.05 [14]
			10.2 ± 0.4 [15]
			10.1 ± 0.4 [16]
SnBr_2	r(Sn–Br) = 2.504 Å; θ = 98.6 ± 0.7° [3]	1.33 [9]	9.0 [12]
	r(Sn–Br) = 2.501 Å; θ = 100.0° [5]		9.83 [12]
	r(Sn–Br) = 2.512 Å; θ = 99.7° [7]		9.87 ± 0.05 [13]
			9.85 ± 0.05 [14]
			10.6 ± 0.2 [17]
			10.0 ± 0.4 [15]
SnI_2	r(Sn–I) = 2.699 Å; θ = 103.5 ± 0.9° [3]	1.74 [9]	9.05 [12]
	r(Sn–I) = 2.688 Å; θ = 105.3° [8]		8.9 [12]
	r(Sn–I) = 2.706 Å [7]		9.8 ± 0.2 [17]
			8.8 ± 0.1 [18]
SnClBr			10.3 ± 0.3 [19]

References

1. Wang, X.; Andrews, L.; Chertihin, G. V.; Souter, P. F. J. Phys. Chem. A 2002, 106, 6302.
2. Hauge, R. H.; Hastie, J. W.; Margrave, J. L. J. Phys. Chem. 1968, 72, 3510.
3. Nasarenko, A. Y.; Spiridonov, V. P.; Butayev, B. S.; Zasorin, E. Z. J. Mol. Struct. 1985, 119, 263.
4. Gershikov, A. G.; Zasorin, E. Z.; Demidov, A. V.; Spiridonov, V. P. Zh. Strukt. Khim. 1986, 27, 36.
5. Ermakov, K. V.; Butayev, B. S.; Spiridonov, V. P. *J. Mol. Struct*. **1991**, *248*, 143.
6. Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc. Dalton Trans.* **1986**, 1551.
7. Demidov, A. V.; Gershikov, A. G.; Zasorin, E. Z.; Spiridonov, V. P. *Zh. Strukt. Khim*. **1983**, *24*, 9.
8. Zmbov, K. F.; Hastie, J. W.; Margrave, J. L. *J. Chem. Soc. Faraday Trans*. **1968**, *64*, 861.
9. Pabst, R. E.; Perry, D. L.; Margrave, J. L.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys*. **1977**, *24*, 323.
10. Novak, I.; Potts, A. W. *J. Chem. Soc. Dalton Trans*. **1983**, 2211.
11. Hastie, J. W.; Zmbov, K. F.; Margrave, J. L. *J. Inorg. Nucl. Chem*. **1968**, *30*, 729.
12. Novak, I.; Potts, A. W. *J. Electron Spectrosc. Relat. Phenom.* **1984**, *33*, 1.
13. Harris, D. H.; Lappert, M. F.; Pedley, J. B.; Sharp, G. J. *J. Chem. Soc. Dalton Trans.* **1976**, 945.
14. Evans, S.; Orchard, A. F. J. *Electron Spectrosc. Relat. Phenom*. **1975**, *6*, 207.
15. Knowles, D. J.; Nicholson, A. J. C.; Swingler, D. L. *J. Phys. Chem*. **1970**, *74*, 3642.
16. Buchanan, A. S.; Knowles, D. J.; Swingler, D. L. *J. Phys. Chem*. **1969**, *73*, 4394.
17. Hirayama, C.; Straw, R. D. *Thermochim. Acta* **1984**, *80*, 297.
18. Hilpert, K.; Gingerich, K. A. *Int. J. Mass Spectrom. Ion Phys*. **1983**, *47*, 247.
19. Ciach, S.; Knowles, D. J.; Nicholson, A. J. C.; Swingler, D. L. *Inorg. Chem*. **1973**, *12*, 1443.