Charge Saturation and Neutral Substitutions in Halomethanes and their Group 14 Analogues

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Supporting Information

Complete Citation for the Gaussian 03 Suite of Programs

Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Table S.1a: Optimized *ab initio* (MP2(full)) and experimental bond distances, a (Å), and bond angles, Θ (°), for the $MH_{4-n}X_n$ molecules (M = C, Si, Ge; X= F, Cl, Br, I.)[†]

	this work	Expt.		this work	Expt.		this work	Expt.
$CH_{4-n}F_n$			**$SiH_{4-n}F_n$**			**$GeH_{4-n}F_n$**		
CH_3F			SiH_3F			GeH_3F		
a_{C-H}	1.090	1.086(2)	a_{Si-H}	1.475	1.47608(19)[a]	a_{Ge-H}	1.530	1.5220(30)[a]
a_{C-F}	1.390	1.383(1)	a_{Si-F}	1.626	1.59450(13)[a]	a_{Ge-F}	1.769	1.7350(10)[a]
Θ_{H-C-H}	110.4	110.2(3)	Θ_{H-Si-H}	110.9	110.63	Θ_{H-Ge-H}	112.8	113.0*
Θ_{F-C-H}	108.6	108.8(3)	Θ_{F-Si-H}	108.0	108.269(21)	Θ_{F-Ge-H}	105.9	105.92(30)
CH_2F_2			SiH_2F_2			GeH_2F_2		
a_{C-H}	1.089	1.084(3)	a_{Si-H}	1.466	1.4652(30)	a_{Ge-H}	1.523	
a_{C-F}	1.360	1.3508(5)	a_{Si-F}	1.608	1.5760(20)	a_{Ge-F}	1.747	
Θ_{H-C-H}	113.7	112.8(3)	Θ_{H-Si-H}	115.3	114,2(3)	Θ_{H-Ge-H}	120.4	
Θ_{F-C-H}	108.6		Θ_{F-Si-H}	108.4		Θ_{F-Ge-H}	107.6	
Θ_{F-C-F}	108.6	108.49(6)	Θ_{F-Si-F}	107.9	107,7(2)	Θ_{F-Ge-F}	105.0	
CHF_3			$SiHF_3$			$GeHF_3$		
a_{C-H}	1.088	1.091(14)	a_{Si-H}	1.454	1.4468(5)	a_{Ge-H}	1.514	
a_{C-F}	1.337	1.3284(31)	a_{Si-F}	1.593	1.5624(1)	a_{Ge-F}	1.725	
Θ_{F-C-H}	110.4		Θ_{F-Si-H}	110.8	110.64(3)	Θ_{F-Ge-H}	112.5	
Θ_{F-C-F}	108.5	108.58(34)	Θ_{F-Si-F}	108.1		Θ_{F-Ge-F}	106.3	
CF_4			SiF_4			GeF_4		
a_{C-F}	1.322	1.319253(3)[a]	a_{Si-F}	1.580	1.554(3)[b]	a_{Ge-F}	1.707	
$CH_{4-n}Cl_n$			**$SiH_{4-n}Cl_n$**			**$GeH_{4-n}Cl_n$**		
CH_3Cl			SiH_3Cl			GeH_3Cl		
a_{C-H}	1.087	1.0854(5)	a_{Si-H}	1.474	1.47496(11)	a_{Ge-H}	1.529	1.5155(11)
a_{C-Cl}	1.778	1.7760(3)	a_{Si-Cl}	2.059	2.05057(6)[a]	a_{Ge-Cl}	2.163	2.14470(17)
Θ_{H-C-H}	110.0	110.35(5)	Θ_{H-Si-H}	110.7		Θ_{H-Ge-H}	112.1	111.0*
Θ_{Cl-C-H}	108.9		$\Theta_{Cl-Si-H}$	108.2	108.295(12)	$\Theta_{Cl-Ge-H}$	106.7	107.10(14)
CH_2Cl_2			SiH_2Cl_2			GeH_2Cl_2		
a_{C-H}	1.086	1.080(3)	a_{Si-H}	1.468	1.4671(50)	a_{Ge-H}	1.525	1.56(2)[b]
a_{C-Cl}	1.767	1.766(2)	a_{Si-Cl}	2.041	2.0316(30)	a_{Ge-Cl}	2.143	2.130(3)[b]
Θ_{H-C-H}	110.9	112.10(20)	Θ_{H-Si-H}	113.3	112.45(50)	Θ_{H-Ge-H}	116.6	
Θ_{Cl-C-H}	108.2		$\Theta_{Cl-Si-H}$	108.4		$\Theta_{Cl-Ge-H}$	108.0	106.4(15)
$\Theta_{Cl-C-Cl}$	113.0	111.96(10)	$\Theta_{Cl-Si-Cl}$	110.1	109.67(30)	$\Theta_{Cl-Ge-Cl}$	108.0	107.2(5)
$CHCl_3$			$SiHCl_3$			$GeHCl_3$		
a_{C-H}	1.085	1.100(5)[c]	a_{Si-H}	1.462	1.464(10)	a_{Ge-H}	1.522	1.55(2)[a]
a_{C-Cl}	1.765	1.758(2)[c]	a_{Si-Cl}	2.028	2.020(3)[a]	a_{Ge-Cl}	2.126	2.1139(50)[a]
Θ_{Cl-C-H}	107.7		$\Theta_{Cl-Si-H}$	109.5	109.5(7)	$\Theta_{Cl-Ge-H}$	110.5	
$\Theta_{Cl-C-Cl}$	111.2	111.3(2)	$\Theta_{Cl-Si-Cl}$	109.5	109.4(3)	$\Theta_{Cl-Ge-Cl}$	108.4	108.3(10)
CCl_4			$SiCl_4$			$GeCl_4$		
a_{C-Cl}	1.771	1.7667(30)[d]	a_{Si-Cl}	2.018	2.0193(34)[d]	a_{Ge-Cl}	2.114	2.113(3)[d]
$CH_{4-n}Br_n$			**$SiH_{4-n}Br_n$**			**$GeH_{4-n}Br_n$**		
CH_3Br			SiH_3Br			GeH_3Br		
a_{C-H}	1.086	1.0823(5)	a_{Si-H}	1.474	1.47425(18)[a]	a_{Ge-H}	1.529	1.527(3)[c]
a_{C-Br}	1.936	1.9340(3)	a_{Si-Br}	2.228	2.21227(9)[a]	a_{Ge-Br}	2.317	2.297(2)[c]
Θ_{H-C-H}	110.6	111.16(5)	Θ_{H-Si-H}	110.7		Θ_{H-Ge-H}	111.9	
Θ_{Br-C-H}	108.3		$\Theta_{Br-Si-H}$	108.2	108.161(20)	$\Theta_{Br-Ge-H}$	106.9	106.3(2)

CH_2Br_2			SiH_2Br_2			GeH_2Br_2		
$a_{C\text{-}H}$	1.085	1.097(5)[c]	$a_{Si\text{-}H}$	1.469		$a_{Ge\text{-}H}$	1.526	1.52(4)
$a_{C\text{-}Br}$	1.929	1.925(2)[c]	$a_{Si\text{-}Br}$	2.211		$a_{Ge\text{-}Br}$	2.299	2.277(3)
$\Theta_{H\text{-}C\text{-}H}$	111.5	110.9(8)	$\Theta_{H\text{-}Si\text{-}H}$	112.8		$\Theta_{H\text{-}Ge\text{-}H}$	115.6	
$\Theta_{Br\text{-}C\text{-}H}$	107.9		$\Theta_{Br\text{-}Si\text{-}H}$	108.3		$\Theta_{Br\text{-}Ge\text{-}H}$	108.0	109.0(21)
$\Theta_{Br\text{-}C\text{-}Br}$	113.8	112.9(2)	$\Theta_{Br\text{-}Si\text{-}Br}$	110.9		$\Theta_{Br\text{-}Ge\text{-}Br}$	109.2	108.4(4)
$CHBr_3$			$SiHBr_3$			$GeHBr_3$		
$a_{C\text{-}H}$	1.085	1.11(5)[d]	$a_{Si\text{-}H}$	1.465	1.494(10)[a]	$a_{Ge\text{-}H}$	1.525	
$a_{C\text{-}Br}$	1.931	1.924(5)[d]	$a_{Si\text{-}Br}$	2.201	2.170(2)[a]	$a_{Ge\text{-}Br}$	2.286	
$\Theta_{Br\text{-}C\text{-}H}$	107.1	107.2(4)	$\Theta_{Br\text{-}Si\text{-}H}$	109.0		$\Theta_{Br\text{-}Ge\text{-}H}$	109.8	
$\Theta_{Br\text{-}C\text{-}Br}$	111.7	111.7(4)	$\Theta_{Br\text{-}Si\text{-}Br}$	110.0	111.36(50)	$\Theta_{Br\text{-}Ge\text{-}Br}$	109.1	
CBr_4			$SiBr_4$			$GeBr_4$		
$a_{C\text{-}Br}$	1.943	1.935*	$a_{Si\text{-}Br}$	2.196	2.183(4)[d]	$a_{Ge\text{-}Br}$	2.279	2.272[d]
$CH_{4-n}I_n$			**$SiH_{4-n}I_n$**			**$GeH_{4-n}I_n$**		
CH_3I			SiH_3I			GeH_3I		
$a_{C\text{-}H}$	1.086	1.084*	$a_{Si\text{-}H}$	1.475	1.4741(14)[a]	$a_{Ge\text{-}H}$	1.530	1.5192(30)[a]
$a_{C\text{-}I}$	2.133	2.132*	$a_{Si\text{-}I}$	2.448	2.43835(59)[a]	$a_{Ge\text{-}I}$	2.521	2.5095(10)[a]
$\Theta_{H\text{-}C\text{-}H}$	111.1	111.2*	$\Theta_{H\text{-}Si\text{-}H}$	110.6		$\Theta_{H\text{-}Ge\text{-}H}$	111.5	
$\Theta_{I\text{-}C\text{-}H}$	107.8		$\Theta_{I\text{-}Si\text{-}H}$	108.3	108.16(17)[a]	$\Theta_{I\text{-}Ge\text{-}H}$	107.4	107.00(30)[a]
CH_2I_2			SiH_2I_2			GeH_2I_2		
$a_{C\text{-}H}$	1.086		$a_{Si\text{-}H}$	1.473		$a_{Ge\text{-}H}$	1.529	
$a_{C\text{-}I}$	2.129		$a_{Si\text{-}I}$	2.435		$a_{Ge\text{-}I}$	2.507	
$\Theta_{H\text{-}C\text{-}H}$	111.6		$\Theta_{H\text{-}Si\text{-}H}$	112.0		$\Theta_{H\text{-}Ge\text{-}H}$	114.1	
$\Theta_{I\text{-}C\text{-}H}$	107.7		$\Theta_{I\text{-}Si\text{-}H}$	108.5		$\Theta_{I\text{-}Ge\text{-}H}$	108.3	
$\Theta_{I\text{-}C\text{-}I}$	114.3		$\Theta_{I\text{-}Si\text{-}I}$	110.8		$\Theta_{I\text{-}Ge\text{-}I}$	109.8	
CHI_3			$SiHI_3$			$GeHI_3$		
$a_{C\text{-}H}$	1.088		$a_{Si\text{-}H}$	1.472		$a_{Ge\text{-}H}$	1.531	
$a_{C\text{-}I}$	2.137		$a_{Si\text{-}I}$	2.428		$a_{Ge\text{-}I}$	2.499	
$\Theta_{I\text{-}C\text{-}H}$	106.6		$\Theta_{I\text{-}Si\text{-}H}$	108.7		$\Theta_{I\text{-}Ge\text{-}H}$	109.3	
$\Theta_{I\text{-}C\text{-}I}$	112.2		$\Theta_{I\text{-}Si\text{-}I}$	110.2		$\Theta_{I\text{-}Ge\text{-}I}$	109.7	
CI_4			SiI_4			GeI_4		
$a_{C\text{-}I}$	2.157	2.15*	$a_{Si\text{-}I}$	2.428		$a_{Ge\text{-}I}$	2.499	2.499

Experimental data are from ref 29. The tetrahalides are of T_d symmetry ($\Theta_{X\text{-}M\text{-}X} = 109.5$).

* $\Theta_{H\text{-}Ge\text{-}H}$ for GeH_3Cl and $a_{C\text{-}Br}$ has been taken from D. R. Lide (Ed) CRC Handbook of Chemistry and Physics 88th ed.,CRC Press Boca Raton, Fl, 2007 (Section 9).

† Unless otherwise stated the bond lengths refer to the distance between the nuclear positions at the potential-energy minimum, a_e. Alternative distance parameters are defined as follows:

[a] a_o; the distance between effective nuclear positions derived from rotational constants in the vibrational ground state.

[b] a_a; the constant argument in the molecular intensity function of electron diffraction, ED, studies.

[c] a_s; the distance between effective nuclear positions derived from isotopic differences in rotational constants.

[d] a_g; the thermal average of the internuclear distance. It is derived from ED and is specific to the temperature of the ED experiment.

Table S.1b: Optimized *ab initio* (MP2(full)) and experimental bond distances, a (Å), and bond angles, Θ (°), for the $MH_{4-n}X_n$ molecules (M = Sn, Pb; X= F, Cl, Br, I).

	MP2	Expt.		MP2	Expt.
$SnH_{4-n}F_n$			**$PbH_{4-n}F_n$**		
SnH_3F			PbH_3F		
a_{Sn-H}	1.701		a_{Pb-H}	1.741	
a_{Sn-F}	1.948		a_{Pb-F}	2.056	
Θ_{H-Sn-H}	113.8		Θ_{H-Pb-H}	116.1	
Θ_{F-Sn-H}	104.7		Θ_{F-Pb-H}	101.5	
SnH_2F_2			PbH_2F_2		
a_{Sn-H}	1.693		a_{Pb-H}	1.723	
a_{Sn-F}	1.929		a_{Pb-F}	2.034	
Θ_{H-Sn-H}	123.2		Θ_{H-Pb-H}	136.5	
Θ_{F-Sn-H}	107.1		Θ_{F-Pb-H}	103.6	
Θ_{F-Sn-F}	103.5		Θ_{F-Pb-F}	101.5	
$SnHF_3$			$PbHF_3$		
a_{Sn-H}	1.683		a_{Pb-H}	1.718	
a_{Sn-F}	1.909		a_{Pb-F}	2.007	
Θ_{F-Sn-H}	113.6		Θ_{F-Pb-H}	116.0	
Θ_{F-Sn-F}	105.1		Θ_{F-Pb-F}	102.2	
SnF_4			PbF_4		
a_{Sn-F}	1.894		a_{Pb-F}	1.993	
$SnH_{4-n}Cl_n$			**$PbH_{4-n}Cl_n$**		
SnH_3Cl			PbH_3Cl		
a_{Sn-H}	1.703	1.696 (5) [a]	a_{Pb-H}	1.742	
a_{Sn-Cl}	2.323	2.328 (5) [a]	a_{Pb-Cl}	2.415	
Θ_{H-Sn-H}	112.5		Θ_{H-Pb-H}	114.6	
$\Theta_{Cl-Sn-H}$	106.2	105.5 (5) [a]	$\Theta_{Cl-Pb-H}$	103.7	
SnH_2Cl_2			PbH_2Cl_2		
a_{Sn-H}	1.698		a_{Pb-H}	1.736	
a_{Sn-Cl}	2.305		a_{Pb-Cl}	2.395	
Θ_{H-Sn-H}	117.6		Θ_{H-Pb-H}	125.4	
$\Theta_{Cl-Sn-H}$	108.1		$\Theta_{Cl-Pb-H}$	106.4	
$\Theta_{Cl-Sn-Cl}$	106.1		$\Theta_{Cl-Pb-Cl}$	104.1	
$SnHCl_3$			$PbHCl_3$		
a_{Sn-H}	1.694		a_{Pb-H}	1.738	
a_{Sn-Cl}	2.289		a_{Pb-Cl}	2.373	
$\Theta_{Cl-Sn-H}$	111.6		$\Theta_{Cl-Pb-H}$	113.0	
$\Theta_{Cl-Sn-Cl}$	107.2		$\Theta_{Cl-Pb-Cl}$	105.7	
$SnCl_4$			$PbCl_4$		
a_{Sn-Cl}	2.276	2.2808 (37) [b]	a_{Pb-Cl}	2.360	2.369(2) [c]
$SnH_{4-n}Br_n$			**$PbH_{4-n}Br_n$**		
SnH_3Br			PbH_3Br		
a_{Sn-H}	1.702		a_{Pb-H}	1.743	
a_{Sn-Br}	2.474	2.4691 (30) [a]	a_{Pb-Br}	2.560	
Θ_{H-Sn-H}	112.3		Θ_{H-Pb-H}	114.2	
$\Theta_{Br-Sn-H}$	106.4	105.9 (20) [a]	$\Theta_{Br-Pb-H}$	104.2	
SnH_2Br_2			PbH_2Br_2		
a_{Sn-H}	1.698		a_{Pb-H}	1.739	
a_{Sn-Br}	2.457		a_{Pb-Br}	2.540	
Θ_{H-Sn-H}	116.8		Θ_{H-Pb-H}	123.3	
$\Theta_{Br-Sn-H}$	108.1		$\Theta_{Br-Pb-H}$	106.7	
$\Theta_{Br-Sn-Br}$	107.2		$\Theta_{Br-Pb-Br}$	105.5	

$SnHBr_3$			$PbHBr_3$	
a_{Sn-H}	1.698		a_{Pb-H}	1.744
a_{Sn-Br}	2.444		a_{Pb-Br}	2.523
$\Theta_{Br-Sn-H}$	110.9		$\Theta_{Br-Pb-H}$	112.1
$\Theta_{Br-Sn-Br}$	108.0		$\Theta_{Br-Pb-Br}$	106.7
$SnBr_4$			$PbBr_4$	
a_{Sn-Br}	2.434		a_{Pb-Br}	2.515
$SnH_{4-n}I_n$			**$PbH_{4-n}I_n$**	
SnH_3I			PbH_3I	
a_{Sn-H}	1.702	1.701 (5) [a]	a_{Pb-H}	1.745
a_{Sn-I}	2.676	2.6746 (50) [a]	a_{Pb-I}	2.752
Θ_{H-Sn-H}	112.0		Θ_{H-Pb-H}	113.6
Θ_{I-Sn-H}	106.8	107.1 (5) [a]	Θ_{I-Pb-H}	104.9
SnH_2I_2			PbH_2I_2	
a_{Sn-H}	1.701		a_{Pb-H}	1.744
a_{Sn-I}	2.663		a_{Pb-I}	2.735
Θ_{H-Sn-H}	115.3		Θ_{H-Pb-H}	120.0
Θ_{I-Sn-H}	108.2		Θ_{I-Pb-H}	107.3
Θ_{I-Sn-I}	108.4		Θ_{I-Pb-I}	106.8
$SnHI_3$			$PbHI_3$	
a_{Sn-H}	1.703		a_{Pb-H}	1.753
a_{Sn-I}	2.654		a_{Pb-I}	2.725
Θ_{I-Sn-H}	110.2		Θ_{I-Pb-H}	111.0
Θ_{I-Sn-I}	108.8		Θ_{I-Pb-I}	107.9
SnI_4			PbI_4	
a_{Sn-I}	2.651		a_{Pb-I}	2.725

The tetrahalides are of T_d symmetry ($\Theta_{X-M-X} = 109.5^o$).

[a] a_o (and θ^o): parameters obtained from the nuclear positions derived from rotational constants in the vibrational ground state. [b] a_g: thermal averages of the internuclear distance, derived from electron diffraction (ED), they are specific to the temperature of the ED experiment (18 ^{o}C for $SnCl_4$). [c] a_a: the bond distance obtained directly from ED experiments (For $PbCl_4$, T = 20 ^{o}C). Note: The Sn—H distances are estimated based on an empirical relationship between a_o(Sn—H) and the vibrational wavenumber ν(Sn—H) for various stannane derivatives. See ref 1 in the footnote below.

[1] Graner, G.; Hirota, E.; Iijima, T.; Kuchitsu, K.; Ramsay, D. A.; Vogt, J.; Vogt N. In Landolt-Börnstein - Numerical Data and Functional Relationships in Science and Technology; Group II: Molecules and Radicals Volume 25. Structure Data of Free Polyatomic Molecules, Sub-volume A: Inorganic Molecules. Martienssen, W., Kuchitsu, K., Eds. Springer-Verlag: Berlin, Heidelberg; 2006.

Table S.2a: CCSD NBO charges for atoms in the $MH_{4-n}X_n$ molecules. The basis sets indicated were used for all elements except Sn, Pb, and I for which we used the pseudoptentials and basis sets used are described in the methods section.

	6-311+G*				6-311++G**				cc-pVTZ				aug-cc-pVTZ			
M = C																
CH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
C	-0.044	-0.518	-0.602	-0.704	-0.022	-0.495	-0.579	-0.681	-0.055	-0.492	-0.570	-0.682	-0.051	-0.507	-0.589	-0.703
H	0.146	0.193	0.200	0.206	0.138	0.184	0.191	0.196	0.141	0.186	0.193	0.197	0.146	0.191	0.197	0.200
X	-0.394	-0.061	0.001	0.087	-0.392	-0.057	0.005	0.092	-0.369	-0.068	-0.009	0.089	-0.386	-0.067	-0.002	0.104
CH_2X_2																
C	0.504	-0.387	-0.556	-0.758	0.522	-0.365	-0.534	-0.735	0.482	-0.330	-0.489	-0.718	0.495	-0.360	-0.529	-0.760
H	0.121	0.201	0.211	0.217	0.110	0.187	0.196	0.202	0.110	0.191	0.198	0.200	0.115	0.195	0.201	0.201
X	-0.373	-0.008	0.066	0.162	-0.371	-0.004	0.070	0.165	-0.351	-0.026	0.047	0.159	-0.363	-0.015	0.064	0.179
CHX_3																
C	0.941	-0.326	-0.583	-0.877	0.952	-0.311	-0.567	-0.862	0.915	-0.235	-0.486	-0.837	0.922	-0.298	-0.562	-0.911
H	0.115	0.208	0.215	0.217	0.099	0.186	0.193	0.196	0.097	0.193	0.190	0.185	0.099	0.195	0.192	0.184
X	-0.352	0.039	0.122	0.220	-0.350	0.042	0.125	0.222	-0.337	0.014	0.099	0.217	-0.340	0.034	0.123	0.243
CX_4																
C	1.326	-0.320	-0.669	-1.048	1.326	-0.320	-0.669	-1.048	1.268	-0.201	-0.572	-1.049	1.277	-0.292	-0.669	-1.142
X	-0.331	0.080	0.167	0.262	-0.331	0.080	0.167	0.262	-0.317	0.050	0.143	0.262	-0.319	0.073	0.167	0.285
M=Si																
SiH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Si	1.282	0.867	0.775	0.660	1.357	0.952	0.863	0.753	1.367	0.996	0.895	0.762	1.385	0.997	0.894	0.751
H	-0.215	-0.166	-0.156	-0.149	-0.240	-0.195	-0.187	-0.181	-0.245	-0.201	-0.192	-0.182	-0.245	-0.200	-0.191	-0.184
X	-0.637	-0.369	-0.306	-0.214	-0.637	-0.367	-0.303	-0.210	-0.632	-0.393	-0.321	-0.215	-0.651	-0.396	-0.320	-0.197
SiH_2X_2																
Si	1.778	1.022	0.844	0.617	1.819	1.073	0.901	0.679	1.834	1.172	0.977	0.708	1.867	1.163	0.959	0.669
H	-0.252	-0.168	-0.152	-0.141	-0.272	-0.195	-0.182	-0.175	-0.283	-0.209	-0.194	-0.182	-0.281	-0.205	-0.191	-0.183
X	-0.637	-0.343	-0.270	-0.168	-0.637	-0.342	-0.269	-0.165	-0.633	-0.377	-0.294	-0.172	-0.652	-0.377	-0.288	-0.152
$SiHX_3$																
.Si	2.171	1.118	0.859	0.515	2.189	1.142	0.887	0.547	2.193	1.292	1.002	0.586	2.248	1.202	0.952	0.510
H	-0.252	-0.165	-0.147	-0.138	-0.289	-0.191	-0.178	-0.175	-0.304	-0.212	-0.199	-0.190	-0.301	-0.170	-0.191	-0.191
X	-0.631	-0.318	-0.237	-0.126	-0.633	-0.317	-0.236	-0.124	-0.630	-0.360	-0.268	-0.132	-0.649	-0.344	-0.254	-0.107
SiX_4																
Si	2.509	1.178	0.835	0.364	2.509	1.178	0.835	0.364	2.490	1.361	0.975	0.393	2.567	1.291	0.902	0.294
X	-0.627	-0.294	-0.209	-0.091	-0.627	-0.294	-0.209	-0.091	-0.623	-0.340	-0.244	-0.098	-0.642	-0.323	-0.226	-0.073
M=Ge																
GeH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Ge	1.155	0.783	0.691	0.535	1.228	0.864	0.775	0.628	1.197	0.848	0.751	0.623	1.216	0.863	0.765	0.624
H	-0.180	-0.132	-0.123	-0.106	-0.204	-0.159	-0.152	-0.139	-0.189	-0.149	-0.141	-0.133	-0.191	-0.152	-0.144	-0.139
X	-0.616	-0.388	-0.321	-0.218	-0.616	-0.386	-0.318	-0.211	-0.631	-0.400	-0.328	-0.223	-0.642	-0.408	-0.332	-0.207
GeH_2X_2																
Ge	1.665	0.973	0.794	0.528	1.702	1.027	0.852	0.589	1.695	1.058	0.870	0.616	1.735	1.066	0.871	0.591
H	-0.210	-0.128	-0.115	-0.096	-0.228	-0.157	-0.147	-0.131	-0.215	-0.150	-0.137	-0.128	-0.216	-0.149	-0.138	-0.133
X	-0.623	-0.358	-0.282	-0.168	-0.623	-0.357	-0.279	-0.164	-0.633	-0.380	-0.298	-0.180	-0.652	-0.384	-0.298	-0.162

$GeHX_3$																
Ge	2.089	1.102	0.838	0.461	2.104	1.127	0.865	0.492	2.105	1.212	0.936	0.552	2.164	1.214	0.921	0.483
H	-0.220	-0.121	-0.107	-0.090	-0.236	-0.148	-0.138	-0.128	-0.225	-0.146	-0.134	-0.130	-0.225	-0.143	-0.133	-0.132
X	-0.623	-0.327	-0.244	-0.124	-0.622	-0.326	-0.242	-0.122	-0.627	-0.356	-0.267	-0.141	-0.646	-0.357	-0.263	-0.117
GeX_4																
Ge	2.467	1.191	0.840	0.351	2.467	1.191	0.840	0.351	2.460	1.329	0.964	0.434	2.542	1.309	0.913	0.334
X	-0.617	-0.298	-0.210	-0.088	-0.617	-0.298	-0.210	-0.088	-0.615	-0.332	-0.241	-0.108	-0.635	-0.327	-0.228	-0.084

M=Sn

SnH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Sn	1.329	0.992	0.908	0.798	1.401	1.070	0.988	0.881	1.409	1.097	1.004	0.882	1.445	1.130	1.039	0.909
H	-0.213	-0.178	-0.170	-0.164	-0.238	-0.205	-0.198	-0.194	-0.243	-0.209	-0.201	-0.194	-0.249	-0.216	-0.209	-0.204
X	-0.689	-0.458	-0.397	-0.306	-0.689	-0.455	-0.393	-0.300	-0.680	-0.472	-0.401	-0.301	-0.697	-0.482	-0.413	-0.297
SnH_2X_2																
Sn	1.847	1.221	1.060	0.846	1.885	1.266	1.108	0.899	1.890	1.319	1.138	0.899	1.932	1.346	1.168	0.915
H	-0.233	-0.174	-0.162	-0.155	-0.253	-0.199	-0.189	-0.185	-0.262	-0.206	-0.194	-0.185	-0.267	-0.210	-0.199	-0.195
X	-0.690	-0.436	-0.368	-0.268	-0.689	-0.434	-0.365	-0.265	-0.683	-0.453	-0.375	-0.265	-0.699	-0.463	-0.385	-0.262
$SnHX_3$																
Sn	2.291	1.391	1.161	0.845	2.306	1.410	1.182	0.873	2.301	1.489	1.223	0.870	2.355	1.513	1.250	0.877
H	-0.240	-0.166	-0.152	-0.148	-0.257	-0.189	-0.178	-0.184	-0.270	-0.199	-0.186	-0.180	-0.272	-0.201	-0.189	-0.190
X	-0.684	-0.408	-0.336	-0.232	-0.683	-0.407	-0.335	-0.230	-0.677	-0.430	-0.346	-0.230	-0.694	-0.437	-0.354	-0.229
SnX_4																
Sn	2.689	1.508	1.217	0.803	2.689	1.508	1.217	0.803	2.663	1.598	1.257	0.803	2.777	1.619	1.279	0.803
X	-0.672	-0.377	-0.304	-0.201	-0.672	-0.377	-0.304	-0.201	-0.666	-0.400	-0.314	-0.201	-0.694	-0.405	-0.320	-0.201

M=Pb

PbH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Pb	1.150	0.848	0.771	0.666	1.216	0.920	0.845	0.743	1.214	0.939	0.854	0.737	1.259	0.976	0.894	0.768
H	-0.153	-0.123	-0.118	-0.114	-0.175	-0.149	-0.144	-0.142	-0.179	-0.151	-0.145	-0.140	-0.186	-0.159	-0.154	-0.152
X	-0.692	-0.478	-0.418	-0.324	-0.690	-0.473	-0.412	-0.316	-0.678	-0.487	-0.420	-0.317	-0.700	-0.499	-0.432	-0.312
PbH_2X_2																
Pb	1.661	1.108	0.962	0.757	1.692	1.147	1.005	0.804	1.688	1.191	1.029	0.800	1.738	1.222	1.062	0.817
H	-0.141	-0.104	-0.098	-0.100	-0.158	-0.127	-0.124	-0.129	-0.166	-0.132	-0.127	-0.127	-0.170	-0.137	-0.133	-0.139
X	-0.690	-0.450	-0.383	-0.279	-0.688	-0.447	-0.378	-0.273	-0.678	-0.463	-0.387	-0.273	-0.699	-0.474	-0.399	-0.270
$PbHX_3$																
Pb	2.110	1.308	1.093	0.788	2.121	1.323	1.111	0.811	2.098	1.388	1.148	0.808	2.161	1.401	1.176	0.814
H	-0.133	-0.090	-0.086	-0.095	-0.147	-0.111	-0.112	-0.127	-0.152	-0.119	-0.117	-0.126	-0.151	-0.118	-0.119	-0.137
X	-0.659	-0.406	-0.335	-0.231	-0.658	-0.404	-0.333	-0.228	-0.649	-0.423	-0.344	-0.227	-0.670	-0.428	-0.352	-0.226
PbX_4																
Pb	2.494	1.448	1.184	0.776	2.494	1.448	1.184	0.776	2.452	1.525	1.218	0.776	2.547	1.552	1.240	0.776
X	-0.623	-0.362	-0.296	-0.194	-0.623	-0.362	-0.296	-0.194	-0.613	-0.381	-0.305	-0.194	-0.637	-0.388	-0.310	-0.194

Table S.2b: MP2 NBO charges for atoms in the $MH_{4-n}X_n$ molecules. The basis sets indicated were used for all elements except Sn, Pb, and I for which we used the pseudoptentials and basis sets used are described in the methods section.

	6-311+G*				6-311++G**				cc-pVTZ				aug-cc-pVTZ			
M = C																
CH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
C	-0.060	-0.536	-0.616	-0.718	-0.042	-0.516	-0.597	-0.700	-0.074	-0.518	-0.591	-0.701	-0.071	-0.527	-0.610	-0.722
H	0.151	0.199	0.207	0.213	0.144	0.192	0.199	0.205	0.146	0.196	0.200	0.205	0.151	0.199	0.204	0.208
X	-0.392	-0.062	-0.004	0.080	-0.390	-0.058	0.001	0.085	-0.365	-0.071	-0.010	0.085	-0.383	-0.069	-0.003	0.099
CH_2X_2																
C	0.495	-0.394	-0.555	-0.753	0.510	-0.375	-0.536	-0.734	0.470	-0.337	-0.497	-0.719	0.482	-0.368	-0.537	-0.760
H	0.123	0.207	0.217	0.224	0.113	0.193	0.203	0.210	0.113	0.198	0.204	0.207	0.118	0.202	0.207	0.208
X	-0.371	-0.009	0.061	0.153	-0.369	-0.006	0.065	0.157	-0.348	-0.029	0.044	0.152	-0.359	-0.017	0.061	0.172
CHX_3																
C	0.933	-0.325	-0.567	-0.851	0.944	-0.311	-0.553	-0.836	0.887	-0.232	-0.481	-0.818	0.911	-0.296	-0.558	-0.891
H	0.117	0.212	0.220	0.223	0.100	0.191	0.198	0.202	0.098	0.198	0.195	0.190	0.101	0.200	0.196	0.188
X	-0.350	0.038	0.116	0.209	-0.348	0.040	0.118	0.211	-0.328	0.011	0.095	0.209	-0.337	0.032	0.121	0.234
CX_4																
C	1.319	-0.312	-0.639	-0.994	1.319	-0.312	-0.639	-0.994	1.257	-0.189	-0.556	-1.012	1.265	-0.283	-0.656	-1.102
X	-0.330	0.078	0.160	0.248	-0.330	0.078	0.160	0.248	-0.314	0.047	0.139	0.253	-0.316	0.071	0.164	0.275
M=Si																
SiH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Si	1.295	0.886	0.796	0.680	1.344	0.953	0.867	0.754	1.364	0.995	0.895	0.764	1.383	0.997	0.894	0.753
H	-0.221	-0.171	-0.161	-0.153	-0.237	-0.194	-0.186	-0.180	-0.246	-0.200	-0.191	-0.181	-0.246	-0.200	-0.191	-0.183
X	-0.632	-0.372	-0.313	-0.221	-0.633	-0.369	-0.309	-0.216	-0.626	-0.394	-0.323	-0.221	-0.646	-0.398	-0.322	-0.203
SiH_2X_2																
Si	1.778	1.033	0.862	0.631	1.803	1.075	0.908	0.683	1.824	1.171	0.976	0.711	1.858	1.161	0.957	0.672
H	-0.257	-0.172	-0.155	-0.144	-0.269	-0.194	-0.181	-0.173	-0.284	-0.208	-0.193	-0.181	-0.282	-0.204	-0.190	-0.181
X	-0.632	-0.345	-0.276	-0.172	-0.632	-0.343	-0.274	-0.168	-0.627	-0.378	-0.295	-0.175	-0.647	-0.377	-0.288	-0.155
$SiHX_3$																
.Si	2.161	1.124	0.873	0.524	2.172	1.144	0.897	0.552	2.176	1.288	0.998	0.587	2.233	1.267	0.946	0.511
H	-0.274	-0.168	-0.150	-0.140	-0.286	-0.191	-0.177	-0.173	-0.305	-0.211	-0.197	-0.188	-0.301	-0.205	-0.190	-0.189
X	-0.629	-0.318	-0.241	-0.128	-0.629	-0.318	-0.240	-0.126	-0.624	-0.359	-0.267	-0.133	-0.644	-0.354	-0.252	-0.107
SiX_4																
Si	2.490	1.178	0.846	0.369	2.490	1.178	0.846	0.369	2.467	1.353	0.967	0.391	2.546	1.317	0.891	0.290
X	-0.622	-0.294	-0.212	-0.092	-0.622	-0.294	-0.212	-0.092	-0.617	-0.338	-0.242	-0.098	-0.636	-0.329	-0.223	-0.072
M=Ge																
GeH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Ge	1.129	0.749	0.658	0.540	1.189	0.815	0.727	0.611	1.183	0.836	0.738	0.612	1.203	0.852	0.753	0.614
H	-0.166	-0.121	-0.113	-0.106	-0.186	-0.144	-0.137	-0.132	-0.186	-0.145	-0.136	-0.128	-0.189	-0.148	-0.140	-0.134
X	-0.632	-0.384	-0.320	-0.223	-0.633	-0.382	-0.316	-0.216	-0.624	-0.401	-0.329	-0.227	-0.636	-0.409	-0.334	-0.212
GeH_2X_2																
Ge	1.646	0.940	0.765	0.531	1.678	0.984	0.813	0.584	1.677	1.049	0.860	0.611	1.719	1.057	0.862	0.585
H	-0.191	-0.117	-0.103	-0.094	-0.207	-0.141	-0.130	-0.125	-0.213	-0.145	-0.132	-0.122	-0.214	-0.145	-0.133	-0.128
X	-0.632	-0.353	-0.279	-0.172	-0.632	-0.351	-0.276	-0.167	-0.625	-0.379	-0.298	-0.183	-0.645	-0.384	-0.298	-0.164

$GeHX_3$																
Ge	2.077	1.070	0.811	0.463	2.090	1.089	0.835	0.490	2.080	1.203	0.928	0.550	2.143	1.205	0.912	0.480
H	-0.198	-0.108	-0.093	-0.087	-0.211	-0.132	-0.121	-0.122	-0.223	-0.140	-0.128	-0.124	-0.223	-0.138	-0.127	-0.127
X	-0.627	-0.321	-0.239	-0.125	-0.626	-0.319	-0.238	-0.123	-0.619	-0.354	-0.267	-0.142	-0.640	-0.356	-0.262	-0.118
GeX_4																
Ge	2.461	1.160	0.818	0.351	2.461	1.160	0.818	0.351	2.429	1.320	0.956	0.433	2.516	1.299	0.902	0.330
X	-0.615	-0.290	-0.204	-0.088	-0.615	-0.290	-0.204	-0.088	-0.607	-0.330	-0.239	-0.108	-0.629	-0.325	-0.225	-0.083
M=Sn																
SnH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Sn	1.337	1.002	0.916	0.805	1.395	1.065	0.982	0.874	1.391	1.082	0.988	0.868	1.429	1.115	1.024	0.896
H	-0.218	-0.181	-0.173	-0.166	-0.238	-0.203	-0.196	-0.191	-0.240	-0.204	-0.196	-0.188	-0.247	-0.211	-0.204	-0.199
X	-0.683	-0.459	-0.398	-0.308	-0.683	-0.455	-0.393	-0.302	-0.670	-0.470	-0.400	-0.303	-0.689	-0.481	-0.412	-0.299
SnH_2X_2																
Sn	1.844	1.225	1.062	0.848	1.875	1.262	1.102	0.893	1.867	1.303	1.124	0.889	1.911	1.331	1.155	0.906
H	-0.238	-0.177	-0.164	-0.155	-0.254	-0.198	-0.187	-0.181	-0.261	-0.201	-0.189	-0.179	-0.265	-0.206	-0.194	-0.190
X	-0.684	-0.436	-0.368	-0.269	-0.683	-0.434	-0.364	-0.265	-0.672	-0.450	-0.373	-0.265	-0.691	-0.459	-0.383	-0.263
$SnHX_3$																
Sn	2.278	1.393	1.155	0.842	2.290	1.408	1.173	0.867	2.270	1.472	1.210	0.863	2.328	1.495	1.236	0.869
H	-0.245	-0.168	-0.153	-0.148	-0.259	-0.187	-0.176	-0.179	-0.270	-0.194	-0.181	-0.175	-0.271	-0.196	-0.183	-0.184
X	-0.678	-0.408	-0.334	-0.232	-0.677	-0.407	-0.333	-0.230	-0.667	-0.426	-0.343	-0.229	-0.686	-0.433	-0.351	-0.228
SnX_4																
Sn	2.665	1.516	1.210	0.796	2.665	1.516	1.210	0.796	2.621	1.584	1.238	0.796	2.706	1.604	1.260	0.796
X	-0.666	-0.379	-0.302	-0.199	-0.666	-0.379	-0.302	-0.199	-0.655	-0.396	-0.310	-0.199	-0.677	-0.401	-0.315	-0.199
M=Pb																
PbH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Pb	1.134	0.833	0.754	0.647	1.189	0.894	0.817	0.712	1.160	0.903	0.817	0.701	1.221	0.941	0.858	0.732
H	-0.150	-0.119	-0.113	-0.108	-0.169	-0.141	-0.136	-0.133	-0.165	-0.140	-0.134	-0.129	-0.178	-0.149	-0.143	-0.141
X	-0.683	-0.476	-0.415	-0.322	-0.681	-0.471	-0.409	-0.313	-0.664	-0.482	-0.415	-0.315	-0.688	-0.494	-0.428	-0.309
PbH_2X_2																
Pb	1.640	1.094	0.944	0.738	1.666	1.128	0.981	0.779	1.637	1.162	0.998	0.772	1.690	1.192	1.032	0.789
H	-0.140	-0.100	-0.093	-0.094	-0.154	-0.120	-0.116	-0.120	-0.155	-0.123	-0.117	-0.116	-0.158	-0.127	-0.122	-0.128
X	-0.680	-0.447	-0.379	-0.275	-0.679	-0.444	-0.375	-0.269	-0.664	-0.458	-0.382	-0.270	-0.687	-0.469	-0.393	-0.266
$PbHX_3$																
Pb	2.082	1.292	1.076	0.771	2.091	1.306	1.092	0.791	2.052	1.359	1.123	0.787	2.121	1.389	1.150	0.794
H	-0.132	-0.085	-0.081	-0.089	-0.143	-0.104	-0.104	-0.118	-0.149	-0.109	-0.107	-0.115	-0.146	-0.109	-0.109	-0.126
X	-0.650	-0.402	-0.332	-0.227	-0.649	-0.401	-0.329	-0.224	-0.634	-0.417	-0.339	-0.224	-0.659	-0.426	-0.347	-0.223
PbX_4																
Pb	2.458	1.447	1.167	0.759	2.458	1.447	1.167	0.759	2.392	1.502	1.196	0.759	2.500	1.524	1.217	0.759
X	-0.615	-0.362	-0.292	-0.190	-0.615	-0.362	-0.292	-0.190	-0.598	-0.376	-0.299	-0.190	-0.625	-0.381	-0.304	-0.190

Table S.2b: B3PW91 NBO charges for atoms in the $MH_{4-n}X_n$ molecules. The basis sets indicated were used for all elements except Sn, Pb, and I for which we used the pseudoptentials and basis sets used are described in the methods section.

	6-311+G*				6-311++G**				cc-pVTZ				aug-cc-pVTZ			
M = C																
CH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
C	-0.085	-0.554	-0.636	-0.740	-0.090	-0.556	-0.638	-0.742	-0.103	-0.544	-0.616	-0.719	-0.108	-0.551	-0.632	-0.737
H	0.158	0.206	0.213	0.217	0.159	0.207	0.214	0.217	0.156	0.205	0.211	0.216	0.161	0.208	0.213	0.216
X	-0.387	-0.064	-0.003	0.091	-0.386	-0.064	-0.003	0.090	-0.365	-0.072	-0.016	0.072	-0.375	-0.073	-0.007	0.088
CH_2X_2																
C	0.473	-0.413	-0.575	-0.785	0.475	-0.408	-0.570	-0.780	0.449	-0.360	-0.512	-0.723	0.449	-0.387	-0.548	-0.769
H	0.130	0.215	0.224	0.228	0.128	0.213	0.221	0.225	0.123	0.212	0.218	0.217	0.127	0.213	0.219	0.219
X	-0.367	-0.009	0.063	0.165	-0.366	-0.008	0.064	0.165	-0.348	-0.032	0.038	0.144	-0.351	-0.019	0.055	0.166
CHX_3																
C	0.915	-0.338	-0.587	-0.898	0.920	-0.328	-0.577	-0.889	0.880	-0.243	-0.486	-0.819	0.881	-0.295	-0.548	-0.887
H	0.122	0.224	0.230	0.229	0.114	0.213	0.219	0.219	0.105	0.214	0.212	0.207	0.105	0.213	0.212	0.206
X	-0.346	0.038	0.119	0.223	-0.345	0.039	0.119	0.223	-0.328	0.010	0.091	0.204	-0.329	0.027	0.112	0.227
CX_4																
C	1.310	-0.320	-0.663	-1.057	1.310	-0.320	-0.663	-1.057	1.232	-0.191	-0.553	-1.013	1.238	-0.268	-0.630	-1.080
X	-0.327	0.080	0.166	0.264	-0.327	0.080	0.166	0.264	-0.308	0.048	0.138	0.253	-0.310	0.067	0.157	0.270
M=Si																
SiH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Si	1.210	0.791	0.693	0.572	1.233	0.815	0.720	0.601	1.254	0.858	0.758	0.641	1.261	0.871	0.767	0.632
H	-0.194	-0.144	-0.133	-0.128	-0.200	-0.152	-0.143	-0.139	-0.207	-0.160	-0.151	-0.144	-0.208	-0.164	-0.154	-0.147
X	-0.629	-0.360	-0.293	-0.189	-0.632	-0.360	-0.290	-0.183	-0.634	-0.377	-0.306	-0.209	-0.638	-0.379	-0.304	-0.190
SiH_2X_2																
Si	1.731	0.954	0.775	0.528	1.738	0.969	0.793	0.550	1.766	1.064	0.883	0.620	1.770	1.053	0.864	0.581
H	-0.233	-0.143	-0.129	-0.122	-0.235	-0.150	-0.138	-0.134	-0.247	-0.171	-0.157	-0.143	-0.247	-0.169	-0.155	-0.145
X	-0.633	-0.334	-0.258	-0.142	-0.634	-0.334	-0.258	-0.141	-0.636	-0.362	-0.285	-0.167	-0.638	-0.358	-0.277	-0.146
$SiHX_3$																
.Si	2.144	1.063	0.795	0.431	2.146	1.069	0.807	0.448	2.165	1.203	0.906	0.537	2.171	1.202	0.882	0.468
H	-0.252	-0.139	-0.122	-0.118	-0.254	-0.145	-0.135	-0.136	-0.270	-0.173	-0.157	-0.148	-0.270	-0.170	-0.151	-0.147
X	-0.631	-0.308	-0.224	-0.104	-0.631	-0.308	-0.224	-0.104	-0.632	-0.343	-0.250	-0.130	-0.634	-0.344	-0.244	-0.107
SiX_4																
Si	2.498	1.134	0.782	0.284	2.498	1.134	0.782	0.284	2.494	1.336	0.942	0.386	2.505	1.291	0.876	0.298
X	-0.624	-0.284	-0.195	-0.071	-0.624	-0.284	-0.195	-0.071	-0.633	-0.334	-0.236	-0.097	-0.626	-0.323	-0.219	-0.075
M=Ge																
GeH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Ge	1.060	0.681	0.589	0.466	1.088	0.715	0.625	0.504	1.074	0.719	0.624	0.505	1.100	0.742	0.648	0.521
H	-0.144	-0.100	-0.093	-0.088	-0.153	-0.112	-0.106	-0.103	-0.150	-0.110	-0.102	-0.095	-0.155	-0.115	-0.108	-0.106
X	-0.627	-0.380	-0.310	-0.201	-0.629	-0.379	-0.308	-0.195	-0.624	-0.389	-0.319	-0.221	-0.633	-0.396	-0.324	-0.205
GeH_2X_2																
Ge	1.590	0.883	0.704	0.458	1.604	0.903	0.724	0.483	1.605	0.953	0.772	0.545	1.628	0.964	0.786	0.506
H	-0.167	-0.093	-0.082	-0.078	-0.173	-0.103	-0.094	-0.094	-0.177	-0.109	-0.096	-0.092	-0.181	-0.111	-0.104	-0.097
X	-0.628	-0.349	-0.270	-0.151	-0.629	-0.349	-0.268	-0.147	-0.625	-0.367	-0.290	-0.180	-0.633	-0.371	-0.289	-0.156

$GeHX_3$																
Ge	2.038	1.028	0.759	0.395	2.042	1.035	0.769	0.408	2.043	1.118	0.858	0.499	2.069	1.117	0.839	0.446
H	-0.173	-0.081	-0.070	-0.071	-0.176	-0.089	-0.081	-0.088	-0.186	-0.101	-0.092	-0.088	-0.190	-0.104	-0.092	-0.094
X	-0.622	-0.315	-0.229	-0.108	-0.622	-0.315	-0.229	-0.107	-0.619	-0.339	-0.255	-0.137	-0.626	-0.338	-0.249	-0.117
GeX_4																
Ge	2.436	1.133	0.773	0.294	2.436	1.133	0.773	0.294	2.421	1.254	0.899	0.417	2.454	1.234	0.855	0.328
X	-0.609	-0.283	-0.193	-0.074	-0.609	-0.283	-0.193	-0.074	-0.605	-0.313	-0.225	-0.104	-0.613	-0.308	-0.214	-0.082
M=Sn																
SnH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Sn	1.276	0.949	0.861	0.744	1.307	0.984	0.898	0.784	1.265	0.946	0.853	0.740	1.314	0.990	0.902	0.782
H	-0.198	-0.162	-0.155	-0.151	-0.209	-0.175	-0.169	-0.166	-0.199	-0.164	-0.156	-0.149	-0.210	-0.176	-0.169	-0.165
X	-0.681	-0.463	-0.395	-0.292	-0.680	-0.460	-0.391	-0.286	-0.668	-0.454	-0.384	-0.292	-0.683	-0.464	-0.396	-0.288
SnH_2X_2																
Sn	1.793	1.183	1.015	0.790	1.806	1.202	1.037	0.816	1.772	1.186	1.009	0.789	1.820	1.218	1.047	0.820
H	-0.215	-0.154	-0.143	-0.139	-0.222	-0.165	-0.157	-0.156	-0.217	-0.159	-0.148	-0.138	-0.225	-0.167	-0.157	-0.157
X	-0.682	-0.438	-0.364	-0.256	-0.681	-0.436	-0.362	-0.252	-0.669	-0.434	-0.357	-0.256	-0.685	-0.442	-0.367	-0.254
$SnHX_3$																
Sn	2.238	1.362	1.119	0.792	2.240	1.368	1.127	0.803	2.204	1.373	1.116	0.796	2.261	1.396	1.148	0.806
H	-0.218	-0.141	-0.130	-0.131	-0.221	-0.149	-0.141	-0.147	-0.222	-0.149	-0.137	-0.135	-0.227	-0.153	-0.147	-0.148
X	-0.673	-0.407	-0.329	-0.220	-0.673	-0.406	-0.329	-0.219	-0.661	-0.408	-0.326	-0.220	-0.678	-0.414	-0.334	-0.219
SnX_4																
Sn	2.633	1.496	1.181	0.746	2.633	1.496	1.181	0.746	2.580	1.518	1.185	0.746	2.660	1.535	1.204	0.746
X	-0.658	-0.374	-0.295	-0.186	-0.658	-0.374	-0.295	-0.186	-0.645	-0.379	-0.296	-0.186	-0.665	-0.384	-0.301	-0.186
M=Pb																
PbH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Pb	1.121	0.836	0.756	0.645	1.148	0.867	0.789	0.679	1.100	0.825	0.742	0.635	1.158	0.876	0.797	0.682
H	-0.147	-0.117	-0.112	-0.110	-0.156	-0.128	-0.125	-0.125	-0.146	-0.117	-0.112	-0.108	-0.159	-0.131	-0.126	-0.125
X	-0.681	-0.485	-0.420	-0.313	-0.681	-0.482	-0.414	-0.305	-0.663	-0.473	-0.406	-0.312	-0.682	-0.484	-0.419	-0.308
PbH_2X_2																
Pb	1.621	1.097	0.945	0.731	1.629	1.112	0.963	0.752	1.587	1.091	0.933	0.725	1.643	1.128	0.975	0.752
H	-0.131	-0.094	-0.090	-0.097	-0.136	-0.103	-0.102	-0.112	-0.132	-0.098	-0.094	-0.094	-0.141	-0.107	-0.104	-0.110
X	-0.679	-0.455	-0.382	-0.269	-0.679	-0.453	-0.379	-0.264	-0.662	-0.448	-0.373	-0.269	-0.681	-0.457	-0.384	-0.266
$PbHX_3$																
Pb	2.064	1.300	1.078	0.763	2.064	1.305	1.084	0.773	2.014	1.302	1.070	0.761	2.079	1.327	1.100	0.773
H	-0.124	-0.077	-0.077	-0.094	-0.123	-0.082	-0.087	-0.110	-0.126	-0.083	-0.083	-0.091	-0.130	-0.088	-0.089	-0.107
X	-0.647	-0.408	-0.333	-0.223	-0.647	-0.407	-0.332	-0.221	-0.630	-0.406	-0.329	-0.223	-0.650	-0.413	-0.337	-0.222
PbX_4																
Pb	2.436	1.460	1.171	0.753	2.436	1.460	1.171	0.753	2.361	1.470	1.170	0.753	2.454	1.488	1.191	0.753
X	-0.609	-0.365	-0.293	-0.188	-0.609	-0.365	-0.293	-0.188	-0.590	-0.367	-0.293	-0.188	-0.614	-0.372	-0.298	-0.188

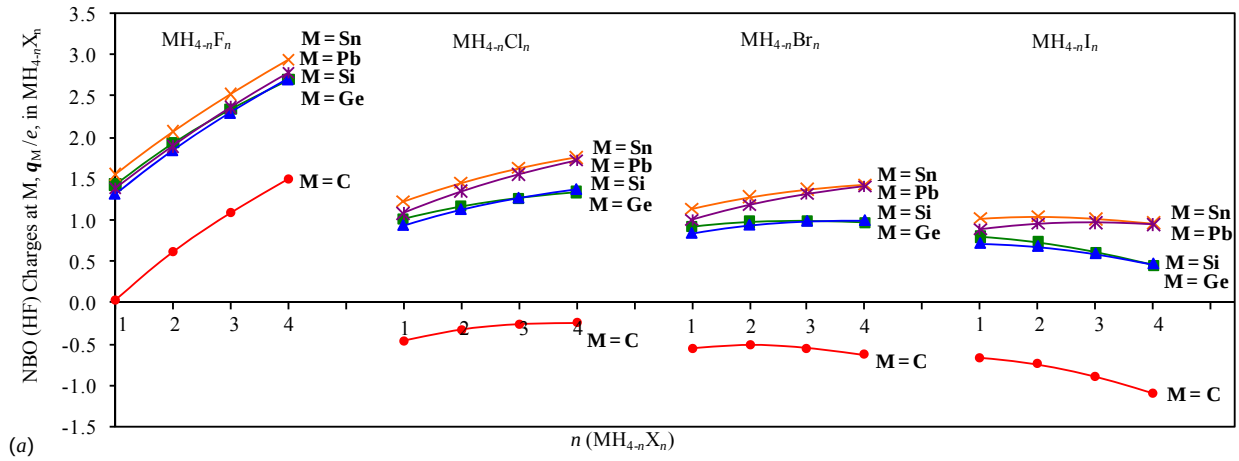
Table S.2b: HF NBO charges for atoms in the $MH_{4-n}X_n$ molecules. The basis sets indicated were used for all elements except Sn, Pb, and I for which we used the pseudoptentials and basis sets used are described in the methods section.

	6-311+G*				6-311++G**				cc-pVTZ				aug-cc-pVTZ			
M = C																
CH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
C	0.033	-0.457	-0.548	-0.664	0.031	-0.457	-0.548	-0.663	0.020	-0.448	-0.533	-0.646	0.009	-0.459	-0.550	-0.664
H	0.134	0.183	0.191	0.195	0.134	0.183	0.191	0.195	0.131	0.181	0.189	0.194	0.137	0.185	0.191	0.195
X	-0.434	-0.091	-0.024	0.080	-0.433	-0.091	-0.024	0.079	-0.413	-0.096	-0.035	0.063	-0.420	-0.097	-0.024	0.080
CH_2X_2																
C	0.613	-0.323	-0.507	-0.743	0.617	-0.317	-0.500	-0.736	0.594	-0.266	-0.441	-0.691	0.594	-0.295	-0.478	-0.729
H	0.110	0.195	0.206	0.208	0.107	0.191	0.202	0.205	0.100	0.189	0.198	0.201	0.104	0.191	0.200	0.200
X	-0.416	-0.033	0.048	0.163	-0.415	-0.033	0.048	0.163	-0.397	-0.056	0.022	0.145	-0.401	-0.044	0.040	0.165
CHX_3																
C	1.081	-0.258	-0.544	-0.891	1.087	-0.250	-0.535	-0.879	1.043	-0.157	-0.432	-0.810	1.048	-0.207	-0.495	-0.872
H	0.105	0.204	0.214	0.211	0.097	0.194	0.203	0.199	0.087	0.194	0.195	0.190	0.088	0.193	0.196	0.191
X	-0.395	0.018	0.110	0.227	-0.395	0.019	0.110	0.227	-0.377	-0.013	0.079	0.207	-0.379	0.005	0.100	0.227
CX_4																
C	1.491	-0.244	-0.630	-1.090	1.415	-0.244	-0.630	-1.090	1.415	-0.109	-0.522	-1.033	1.418	-0.199	-0.603	-1.100
X	-0.373	0.061	0.158	0.272	-0.354	0.061	0.158	0.272	-0.354	0.027	0.131	0.258	-0.355	0.050	0.151	0.275
M=Si																
SiH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Si	1.430	1.013	0.916	0.795	1.450	1.040	0.946	0.827	1.475	1.104	1.003	0.877	1.494	1.099	1.002	0.869
H	-0.249	-0.201	-0.192	-0.187	-0.255	-0.210	-0.201	-0.198	-0.263	-0.226	-0.215	-0.207	-0.269	-0.224	-0.216	-0.210
X	-0.683	-0.409	-0.341	-0.234	-0.684	-0.411	-0.342	-0.233	-0.686	-0.427	-0.356	-0.256	-0.688	-0.427	-0.354	-0.240
SiH_2X_2																
Si	1.933	1.165	0.977	0.727	1.941	1.188	1.004	0.759	1.969	1.282	1.087	0.828	1.971	1.285	1.066	0.793
H	-0.282	-0.198	-0.183	-0.178	-0.285	-0.209	-0.197	-0.194	-0.298	-0.230	-0.215	-0.204	-0.297	-0.226	-0.213	-0.204
X	-0.684	-0.384	-0.305	-0.186	-0.685	-0.385	-0.306	-0.185	-0.687	-0.411	-0.328	-0.210	-0.688	-0.417	-0.320	-0.192
$SiHX_3$																
.Si	2.344	1.268	0.988	0.608	2.347	1.279	1.003	0.627	2.363	1.438	1.141	0.732	2.367	1.413	1.099	0.667
H	-0.300	-0.194	-0.176	-0.174	-0.301	-0.204	-0.190	-0.193	-0.318	-0.232	-0.217	-0.209	-0.317	-0.227	-0.212	-0.205
X	-0.682	-0.358	-0.270	-0.145	-0.682	-0.359	-0.271	-0.144	-0.682	-0.402	-0.308	-0.174	-0.683	-0.395	-0.296	-0.154
SiX_4																
Si	2.700	1.337	0.970	0.455	2.700	1.337	0.970	0.455	2.692	1.541	1.132	0.551	2.698	1.501	1.069	0.470
X	-0.675	-0.334	-0.243	-0.114	-0.675	-0.334	-0.243	-0.114	-0.673	-0.385	-0.283	-0.138	-0.675	-0.375	-0.267	-0.118
M=Ge																
GeH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Ge	1.316	0.935	0.839	0.717	1.350	0.975	0.877	0.754	1.342	0.986	0.887	0.780	1.365	1.022	0.922	0.773
H	-0.208	-0.166	-0.157	-0.154	-0.218	-0.179	-0.171	-0.169	-0.217	-0.179	-0.170	-0.169	-0.222	-0.189	-0.181	-0.173
X	-0.693	-0.438	-0.367	-0.254	-0.695	-0.438	-0.364	-0.246	-0.693	-0.449	-0.376	-0.274	-0.700	-0.453	-0.378	-0.255
GeH_2X_2																
Ge	1.845	1.129	0.939	0.680	1.862	1.150	0.964	0.708	1.867	1.205	1.015	0.762	1.887	1.212	1.015	0.737
H	-0.229	-0.158	-0.146	-0.142	-0.236	-0.168	-0.158	-0.158	-0.240	-0.179	-0.166	-0.157	-0.244	-0.181	-0.169	-0.163
X	-0.694	-0.406	-0.324	-0.198	-0.695	-0.407	-0.324	-0.196	-0.694	-0.424	-0.341	-0.224	-0.699	-0.425	-0.339	-0.205

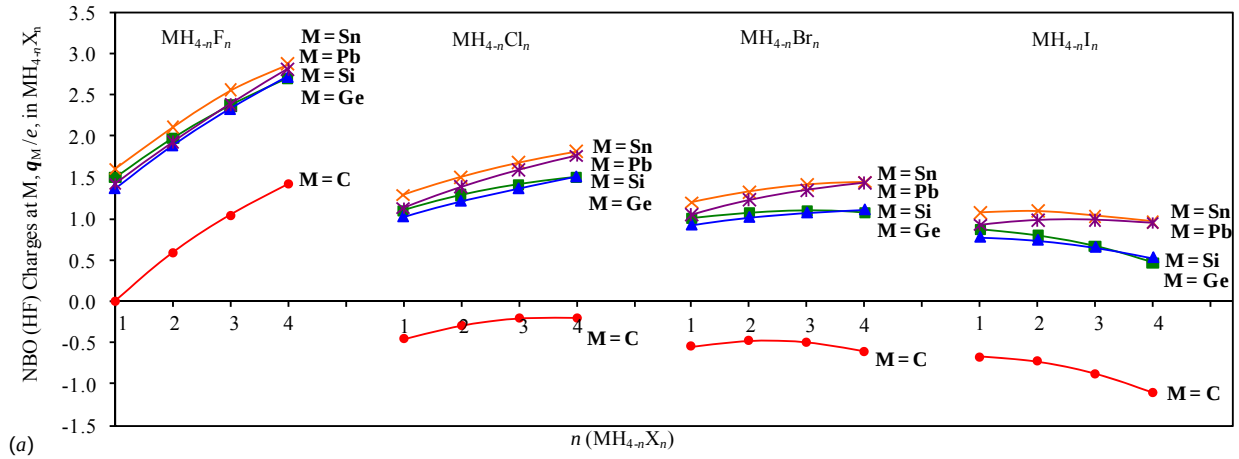
$GeHX_3$																
Ge	2.299	1.268	0.986	0.591	2.305	1.280	1.001	0.610	2.310	1.367	1.088	0.700	2.330	1.364	1.069	0.650
H	-0.235	-0.147	-0.134	-0.136	-0.240	-0.159	-0.150	-0.157	-0.249	-0.173	-0.161	-0.157	-0.253	-0.174	-0.162	-0.161
X	-0.688	-0.374	-0.284	-0.152	-0.688	-0.374	-0.284	-0.151	-0.687	-0.398	-0.309	-0.181	-0.692	-0.397	-0.302	-0.163
GeX_4																
Ge	2.706	1.373	0.995	0.468	2.706	1.373	0.995	0.468	2.700	1.492	1.123	0.607	2.721	1.509	1.107	0.525
X	-0.677	-0.343	-0.249	-0.117	-0.677	-0.343	-0.249	-0.117	-0.675	-0.373	-0.281	-0.152	-0.680	-0.377	-0.277	-0.131
M=Sn																
SnH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Sn	1.558	1.229	1.139	1.021	1.591	1.265	1.178	1.062	1.561	1.234	1.139	1.041	1.602	1.287	1.196	1.070
H	-0.270	-0.235	-0.228	-0.223	-0.281	-0.248	-0.242	-0.238	-0.273	-0.238	-0.231	-0.230	-0.283	-0.254	-0.247	-0.241
X	-0.748	-0.523	-0.456	-0.351	-0.748	-0.521	-0.453	-0.347	-0.742	-0.519	-0.478	-0.351	-0.752	-0.525	-0.456	-0.347
SnH_2X_2																
Sn	2.071	1.452	1.279	1.046	2.086	1.473	1.303	1.074	2.070	1.477	1.294	1.064	2.106	1.504	1.327	1.087
H	-0.286	-0.227	-0.215	-0.210	-0.294	-0.238	-0.228	-0.227	-0.291	-0.239	-0.227	-0.219	-0.298	-0.247	-0.236	-0.232
X	-0.750	-0.499	-0.425	-0.313	-0.749	-0.498	-0.423	-0.310	-0.744	-0.499	-0.420	-0.313	-0.755	-0.505	-0.428	-0.311
$SnHX_3$																
Sn	2.524	1.629	1.372	1.019	2.529	1.637	1.381	1.031	2.516	1.655	1.371	1.026	2.553	1.676	1.412	1.033
H	-0.293	-0.216	-0.204	-0.204	-0.297	-0.225	-0.214	-0.219	-0.299	-0.231	-0.215	-0.210	-0.304	-0.237	-0.224	-0.220
X	-0.744	-0.471	-0.389	-0.272	-0.744	-0.471	-0.389	-0.271	-0.739	-0.475	-0.385	-0.272	-0.750	-0.480	-0.396	-0.271
SnX_4																
Sn	2.937	1.762	1.431	0.963	2.937	1.762	1.431	0.963	2.916	1.792	1.422	0.963	2.869	1.809	1.440	0.963
X	-0.734	-0.440	-0.358	-0.241	-0.734	-0.440	-0.358	-0.241	-0.729	-0.448	-0.355	-0.241	-0.742	-0.452	-0.360	-0.241
M=Pb																
PbH_3X	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I	**X=F**	**X=Cl**	**X=Br**	**X=I**	X=F	X=Cl	X=Br	X=I
Pb	1.384	1.086	1.003	0.888	1.412	1.118	1.037	0.923	1.375	1.084	0.997	0.881	1.422	1.129	1.046	0.924
H	-0.210	-0.180	-0.174	-0.172	-0.219	-0.191	-0.187	-0.186	-0.210	-0.182	-0.175	-0.170	-0.221	-0.194	-0.188	-0.185
X	-0.756	-0.547	-0.481	-0.371	-0.755	-0.544	-0.477	-0.365	-0.746	-0.540	-0.471	-0.371	-0.759	-0.548	-0.481	-0.367
PbH_2X_2																
Pb	1.896	1.345	1.184	0.955	1.906	1.362	1.205	0.979	1.883	1.350	1.182	0.961	1.923	1.382	1.226	0.986
H	-0.193	-0.155	-0.149	-0.155	-0.199	-0.164	-0.161	-0.171	-0.196	-0.160	-0.154	-0.158	-0.203	-0.168	-0.167	-0.172
X	-0.754	-0.518	-0.443	-0.323	-0.754	-0.517	-0.441	-0.319	-0.746	-0.515	-0.437	-0.323	-0.759	-0.523	-0.446	-0.321
$PbHX_3$																
Pb	2.364	1.552	1.314	0.971	2.365	1.557	1.323	0.983	2.343	1.564	1.319	0.975	2.386	1.587	1.346	0.986
H	-0.181	-0.136	-0.135	-0.151	-0.181	-0.143	-0.145	-0.168	-0.185	-0.143	-0.145	-0.155	-0.186	-0.148	-0.152	-0.168
X	-0.728	-0.472	-0.393	-0.273	-0.728	-0.472	-0.393	-0.272	-0.719	-0.474	-0.391	-0.274	-0.733	-0.480	-0.398	-0.273
PbX_4																
Pb	2.777	1.719	1.409	0.950	2.777	1.719	1.409	0.950	2.740	1.740	1.412	0.950	2.808	1.758	1.433	0.950
X	-0.694	-0.430	-0.352	-0.237	-0.694	-0.430	-0.352	-0.237	-0.685	-0.435	-0.353	-0.237	-0.702	-0.439	-0.358	-0.237

Figures

Charges plotted for the Central atoms (q_M) for two sample cases: 6-311+G* and aug-cc-pVTZ for all four methods.

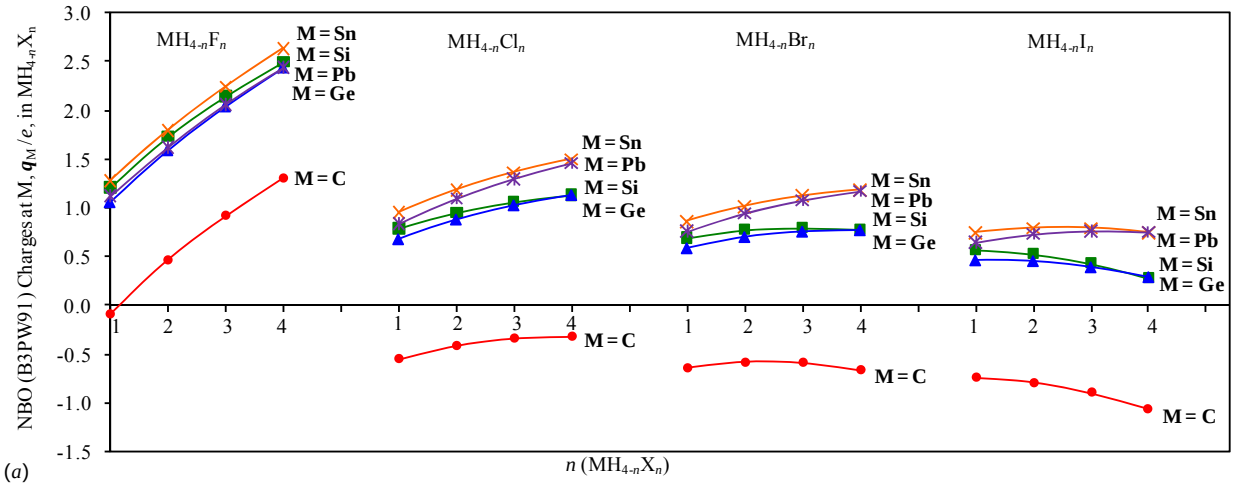


Basis Set: 6-311+G*

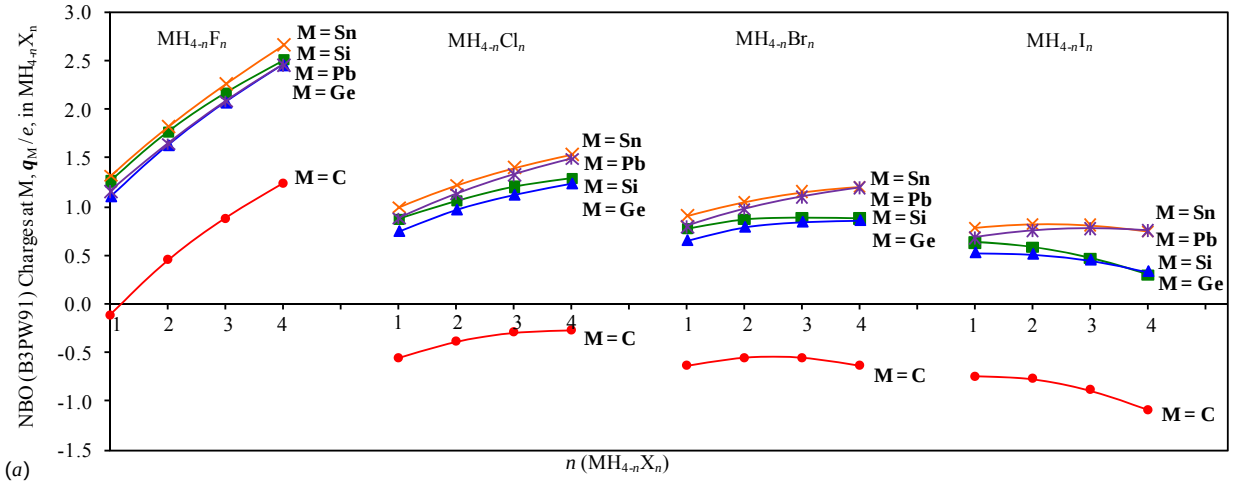


Basis Set: aug-cc-pVTZ

Figure S.1a: *NBO point charges obtained at the HF level of theory for the central atoms, q_M. The q_X data plotted below and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

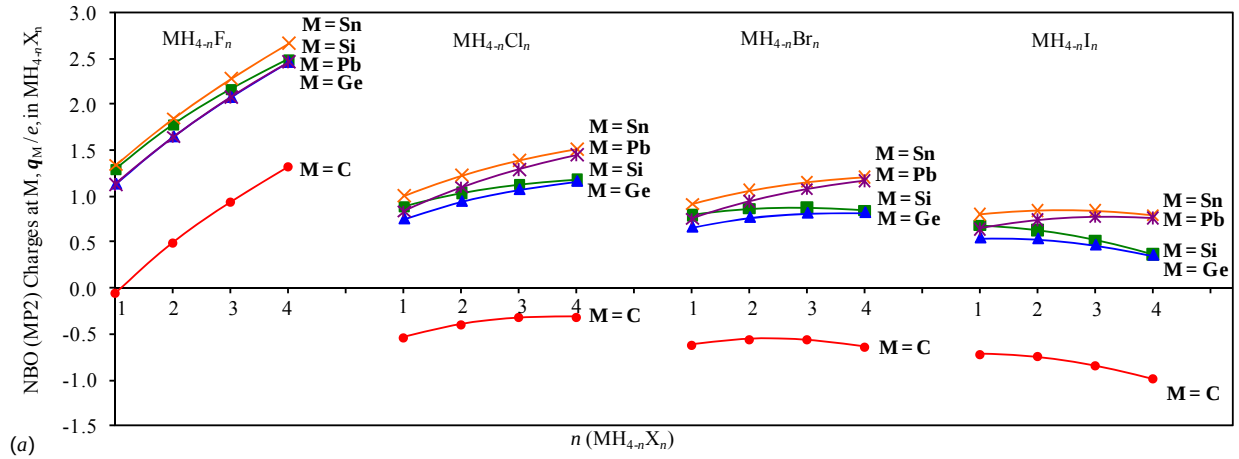


Basis Set: 6-311+G*

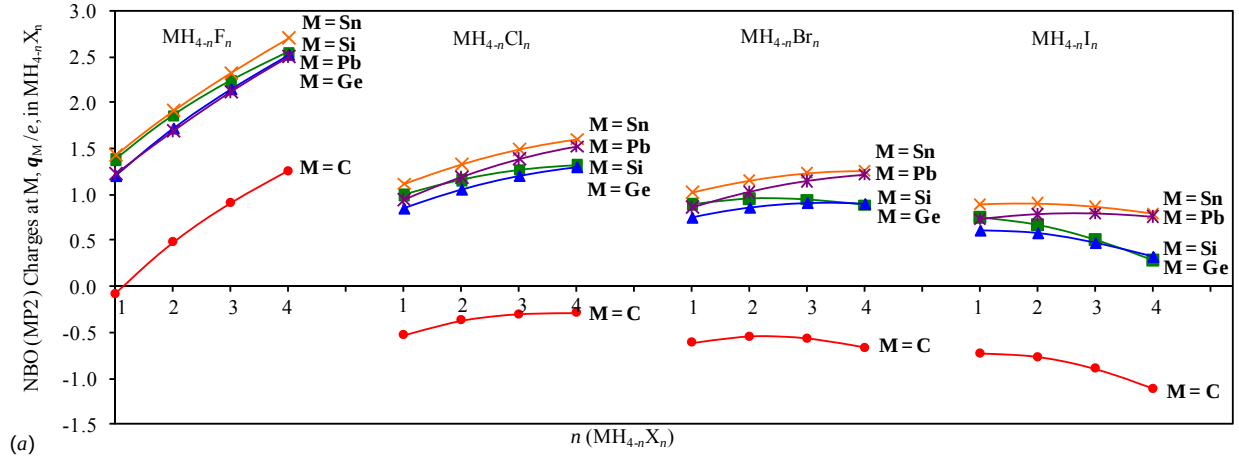


Basis Set: aug-cc-pVTZ

Figure S.1b: *NBO point charges obtained at the B3PW91 level of theory for the central atoms, q_M. The q_X data plotted below and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

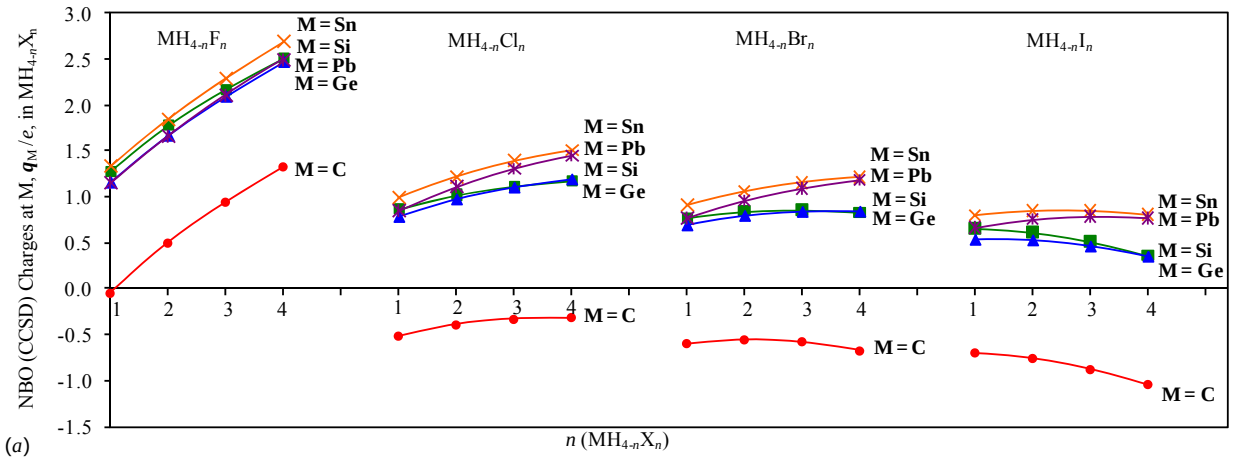


Basis Set: 6-311+G*

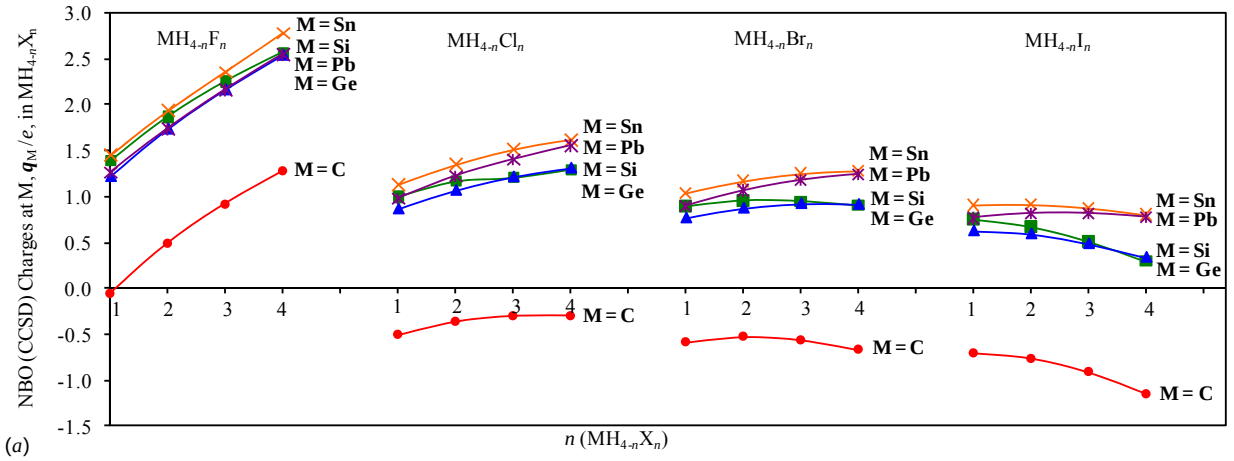


Basis Set: aug-cc-pVTZ

Figure S.1c: *NBO point charges obtained at the MP2(full) level of theory for the central atoms, q_M. The q_X data plotted below and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*



Basis Set: 6-311+G*



Basis Set: aug-cc-pVTZ

Figure S.1d: *NBO point charges obtained at the CCSD level of theory for the central atoms, q_M. The q_X data plotted below and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

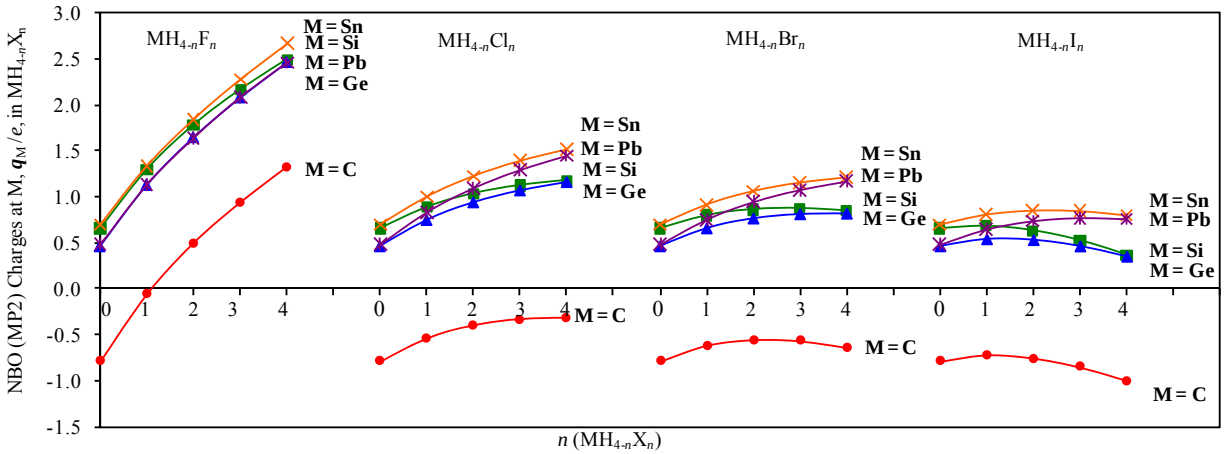


Figure S.1e: *NBO point charges obtained at the MP2(full) level of theory for the central atoms, q_M, extended to include the MH_4 (n = 0) molecules.. For the elements preceding Sn in the periodic table, the* 6-311+G* *basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section. The additional tetrahydride charges are given below.*

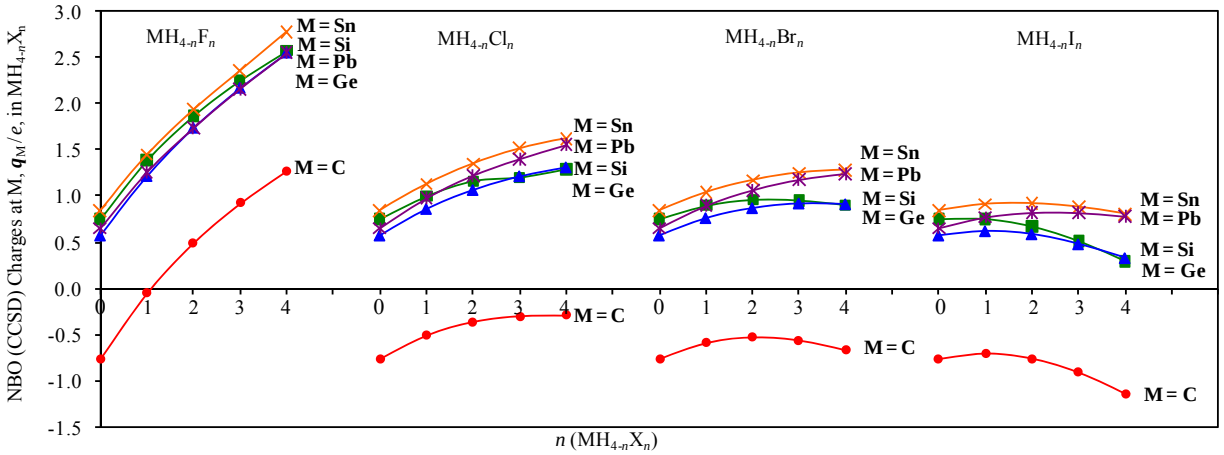
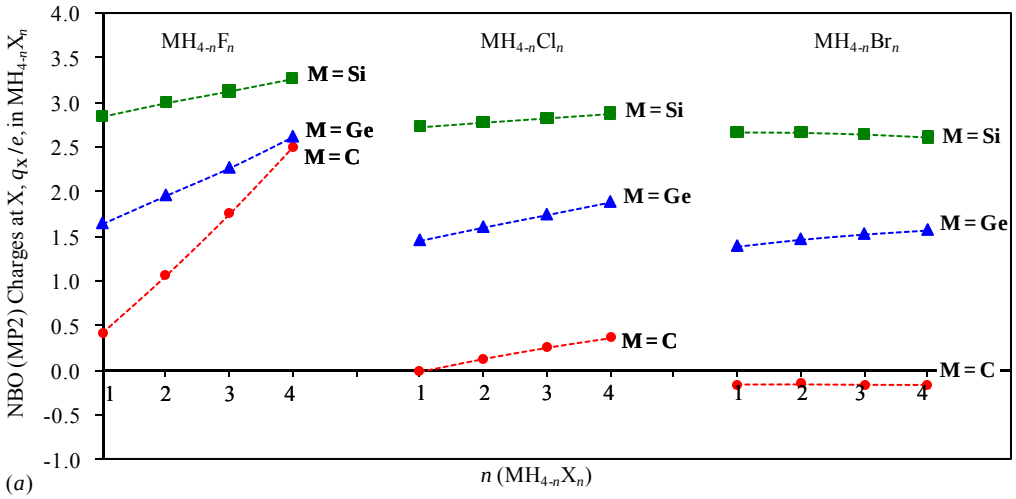


Figure S.1f: *NBO point charges obtained at the CCSD level of theory for the central atoms, q_M, extended to include the MH_4 (n = 0) molecules. For the elements preceding Sn in the periodic table, the* aug-cc-pVTZ *basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section. The additional tetrahydride charges are given below.*

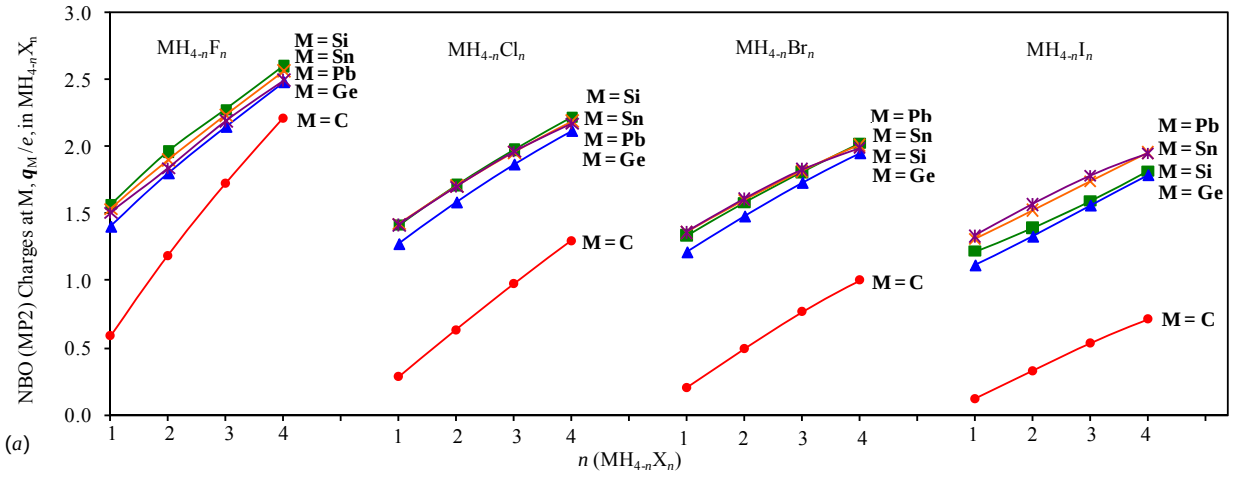
	MP2(full)/6-311+G*	CCSD/aug-cc-pVTZ
CH_4		
C	-0.790	-0.762
H	0.198	0.190
SiH_4		
Si	0.654	0.750
H	-0.163	-0.188
GeH_4		
Ge	0.464	0.577
H	-0.116	-0.144

	MP2(full)/6-311+G*	CCSD/aug-cc-pVTZ
SnH_4		
Sn	0.696	0.843
H	-0.174	-0.211
PbH_4		
Pb	0.480	0.652
H	-0.120	-0.163



Basis Set: 6-311+G*

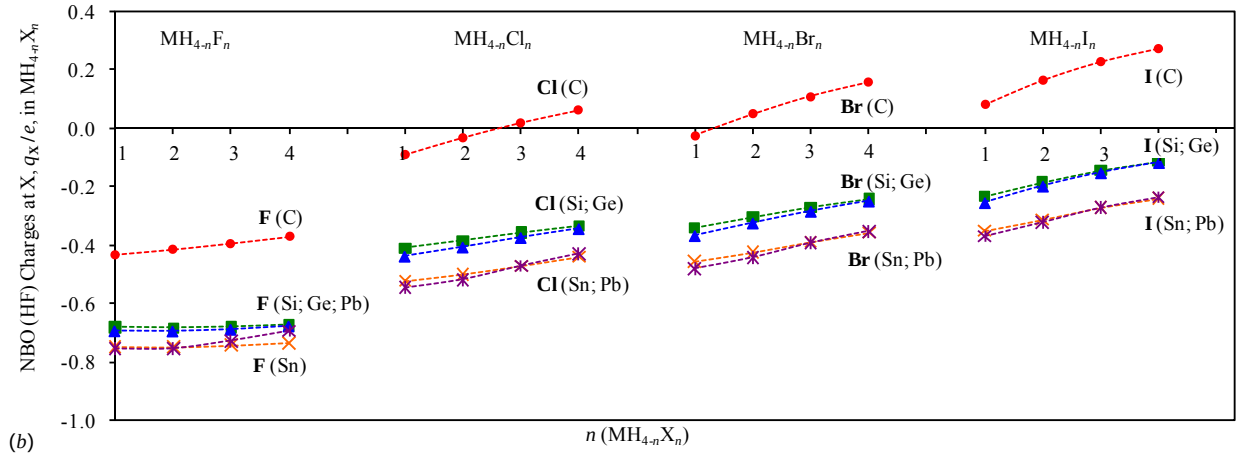
Figure S.2a: ***AIM*** *point charges obtained at the MP2(full) level of theory for the central atoms, q_M. The q_X data plotted below and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*



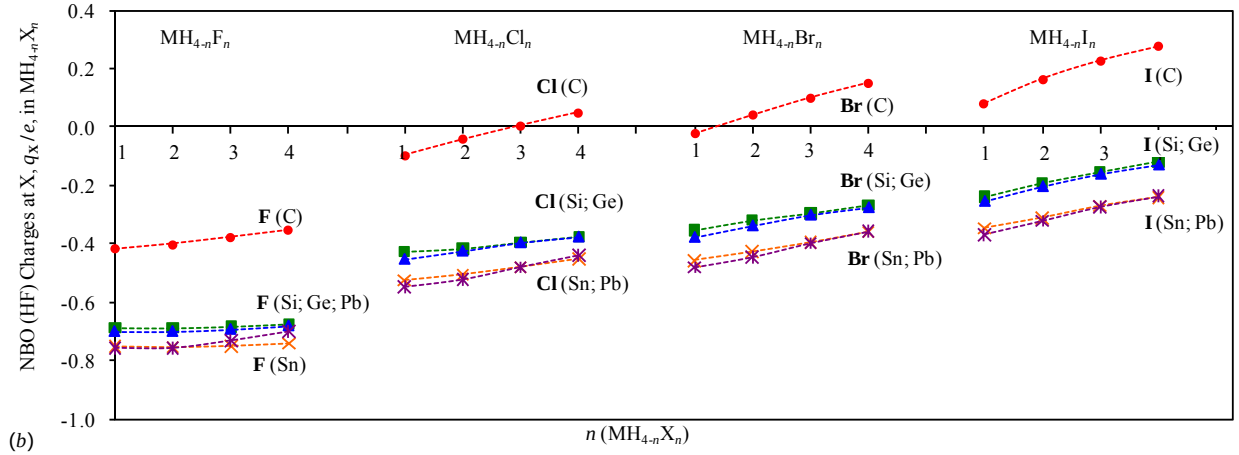
Basis Set: 6-311+G*

Figure S.2b: ***APT*** *point charges obtained at the MP2(full) level of theory for the central atoms, q_M. The q_X data plotted below and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

Charges plotted for the terminal atoms (q_X) for two sample cases: 6-311+G* and aug-cc-pVTZ for all four methods.

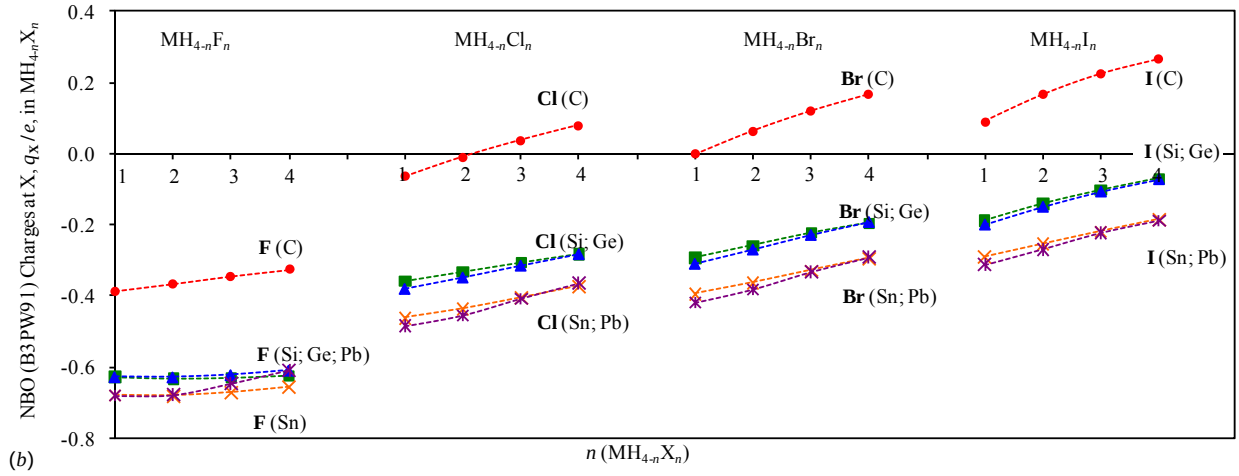


Basis Set: 6-311+G*

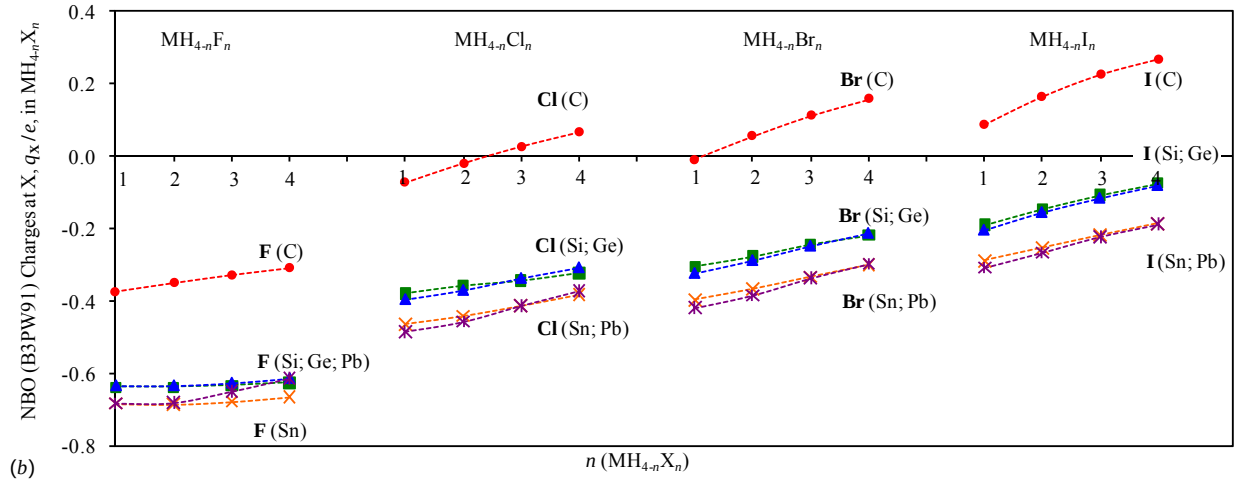


Basis Set: aug-cc-pVTZ

Figure S.3a*: NBO point charges obtained at the HF level of theory for the terminal atoms, q_X. The q_M data plotted above and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

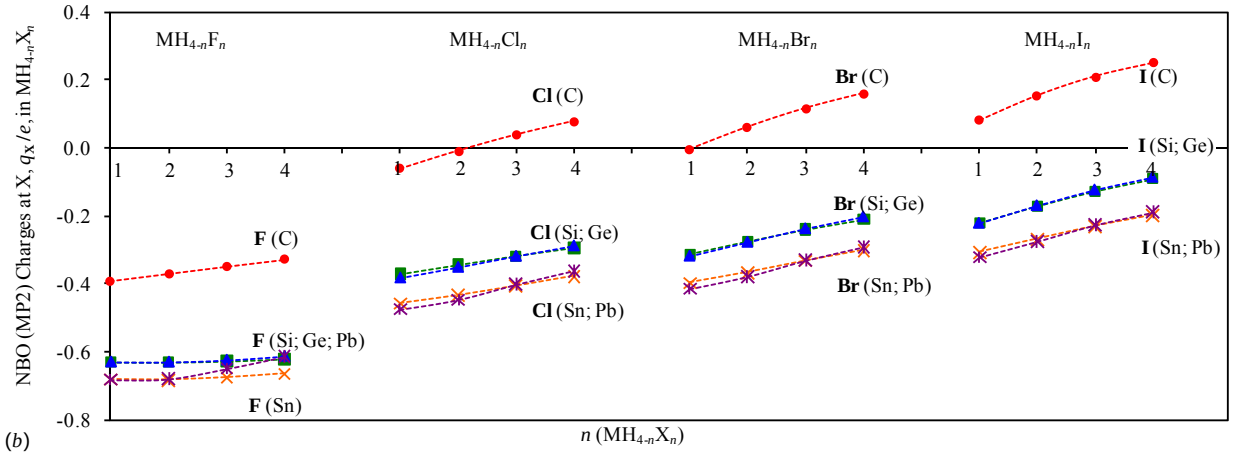


Basis Set: 6-311+G*



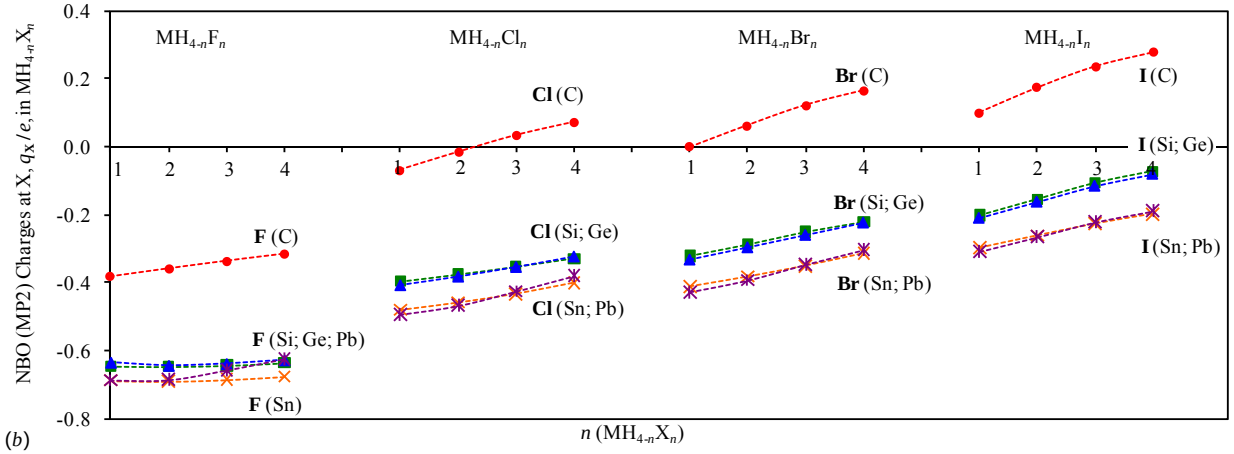
Basis Set: aug-cc-pVTZ

Figure S.3b*: NBO point charges obtained at the B3PW91 level of theory for the terminal atoms, q_X. The q_M data plotted above and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*



(*b*)

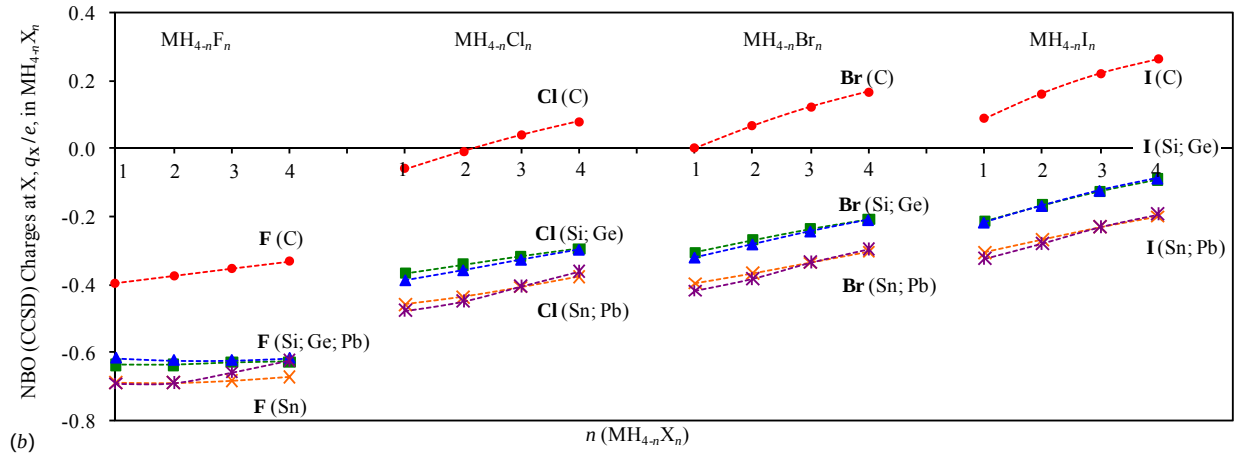
Basis Set: 6-311+G*



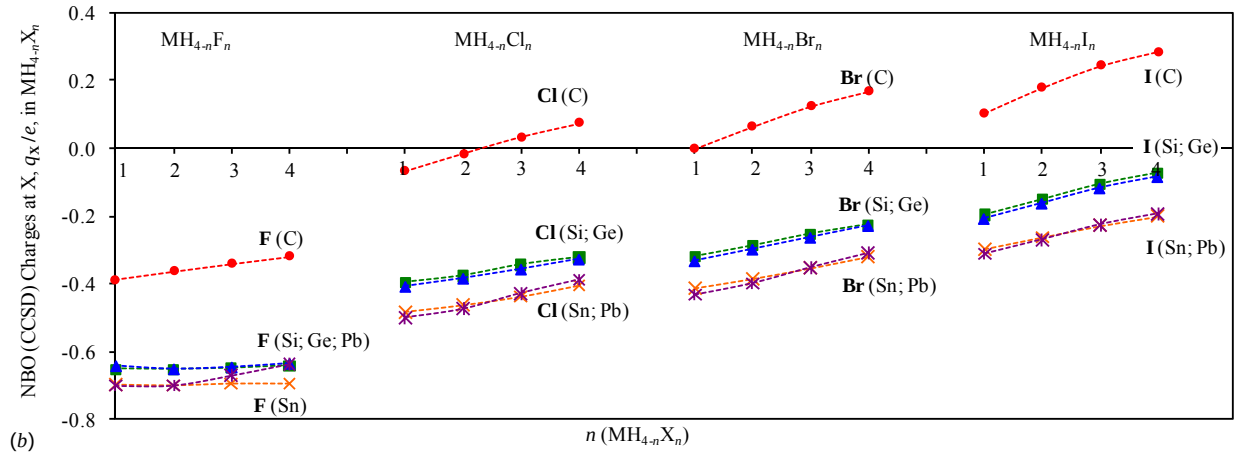
(*b*)

Basis Set: aug-cc-pVTZ

Figure S.3c: *NBO point charges obtained at the MP2(full) level of theory for the terminal atoms, q_X. The q_M data plotted above and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

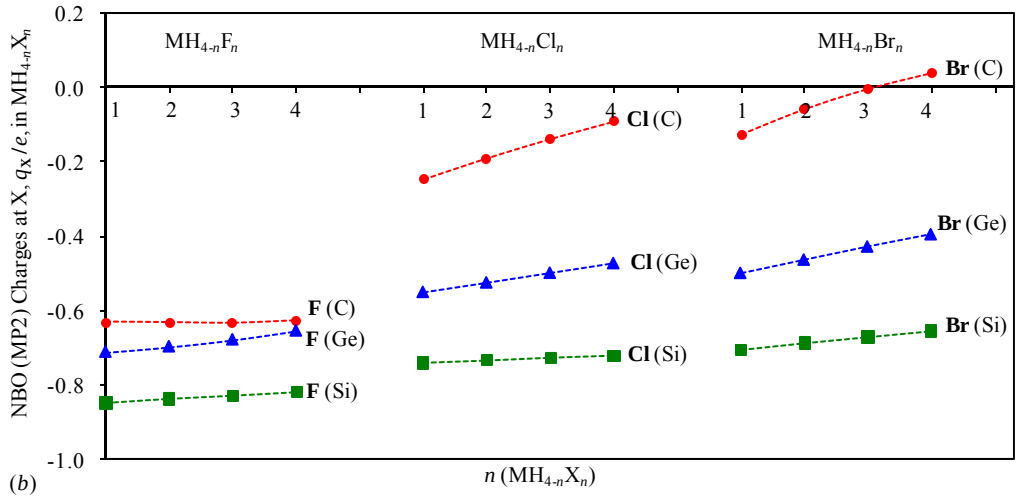


Basis Set: 6-311+G*



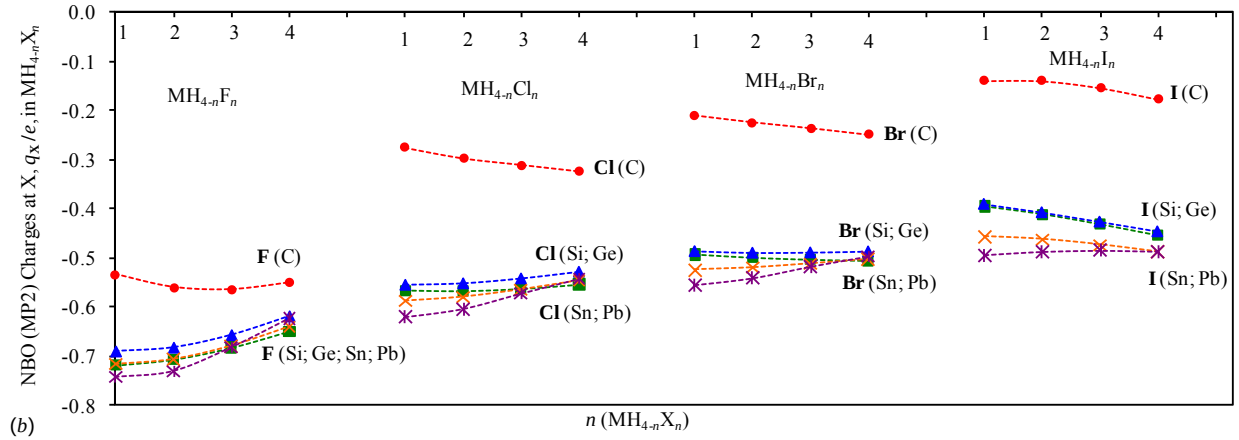
Basis Set: aug-cc-pVTZ

Figure S.3d: *NBO point charges obtained at the CCSD level of theory for the terminal atoms, q_X. The q_M data plotted above and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*



Basis Set: 6-311+G*

Figure S.4a*: AIM point charges obtained at the CCSD level of theory for the terminal atoms, q_X. The q_M data plotted above and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*



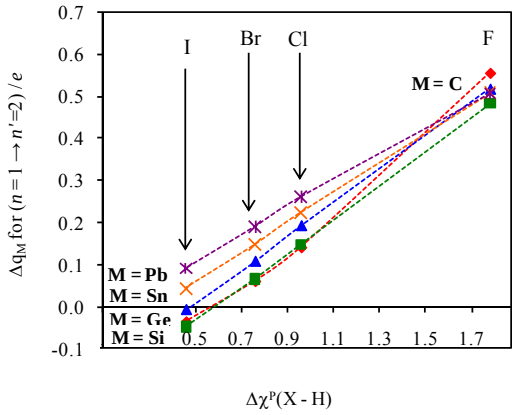
Basis Set: 6-311+G*

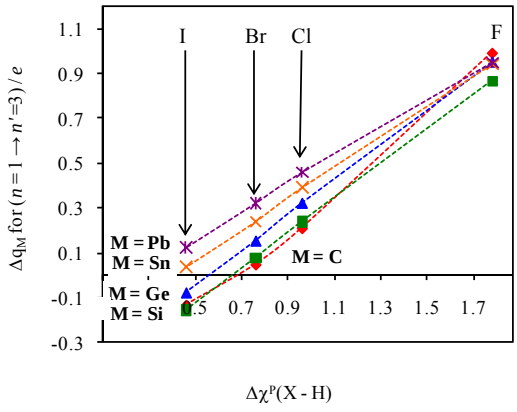
Figure S.4b*: APT point charges obtained at the CCSD level of theory for the terminal atoms, q_X. The q_M data plotted above and the corresponding q_H values are all listed in the tables in the supporting information. For the elements preceding Sn in the periodic table, the stated basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

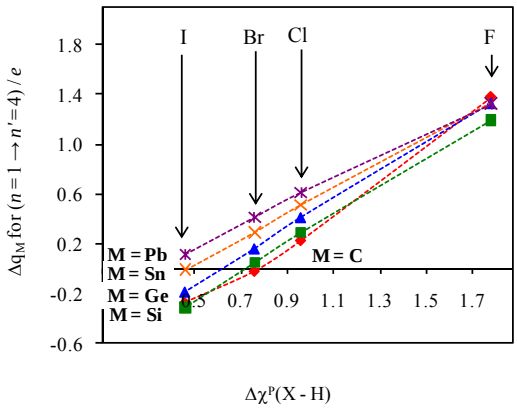
Sample plots of the equation $([q_{M(n')} - q_{M(n)}] = a[\chi_{A'} - \chi_A] + b)$ **[*Figure S.5*]**

MP2 (NBO)

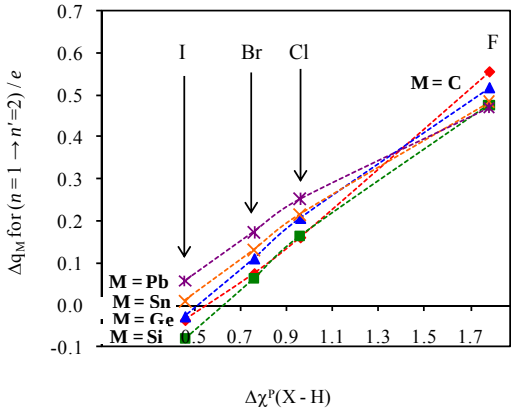
Basis Set: 6-311+G*

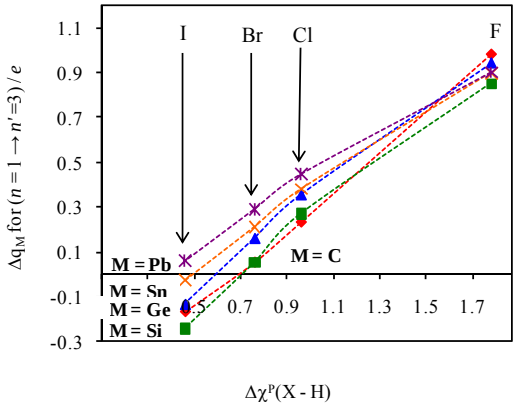


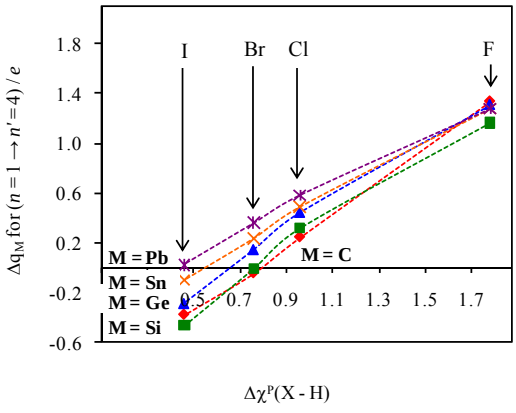




Basis Set aug-cc-pVTZ

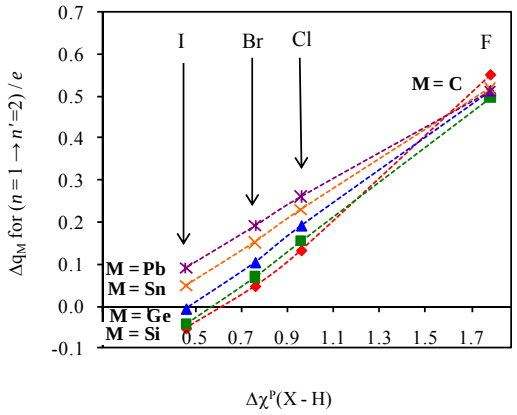


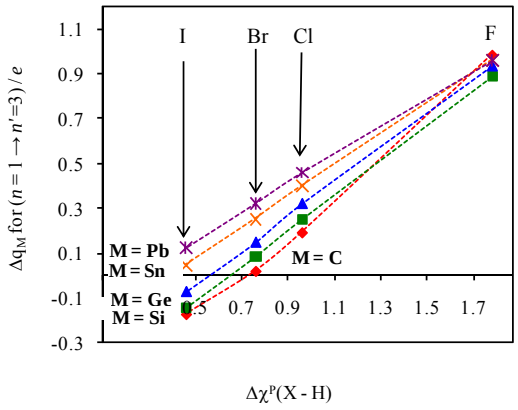


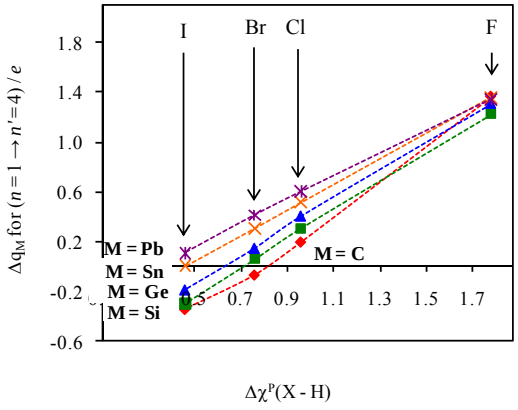


CCSD (NBO)

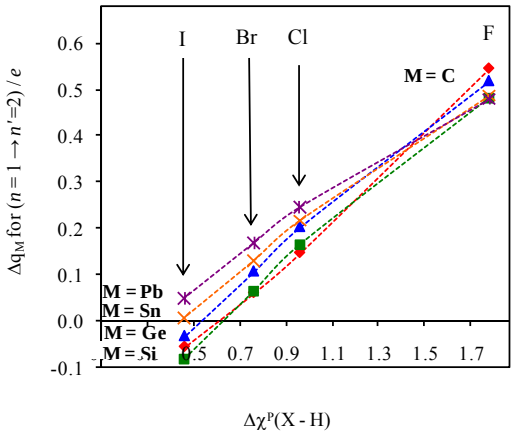
Basis Set: 6-311+G*

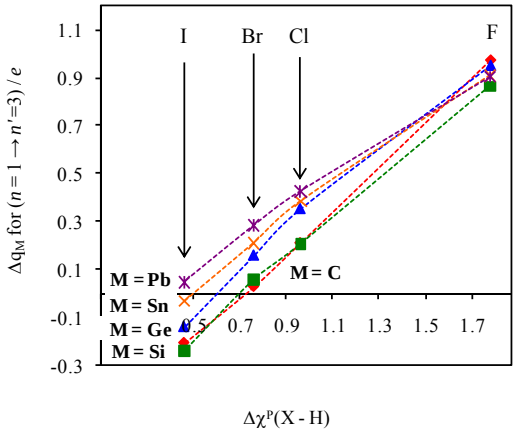


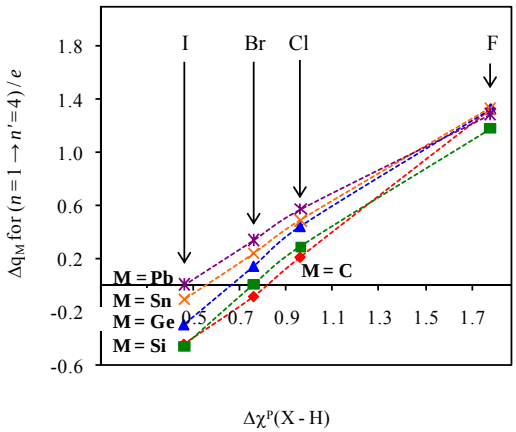




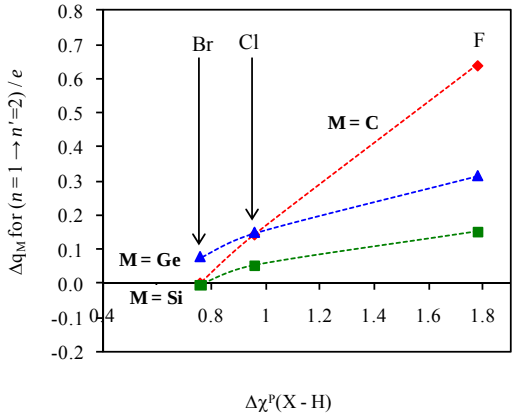
Basis Set aug-cc-pVTZ

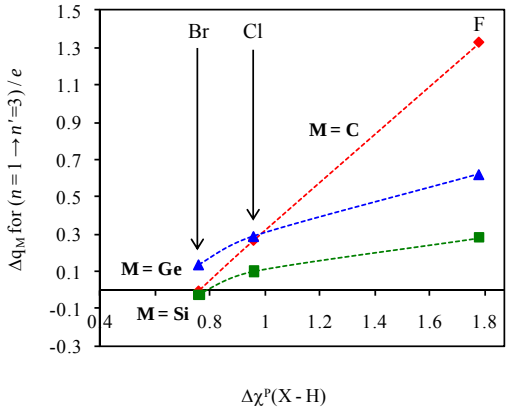


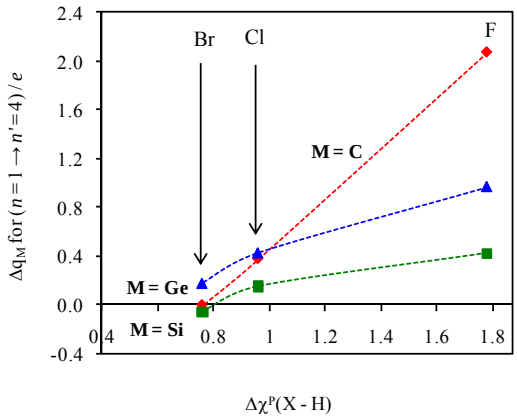




MP2 (AIM) Basis Set: 6-311+G*

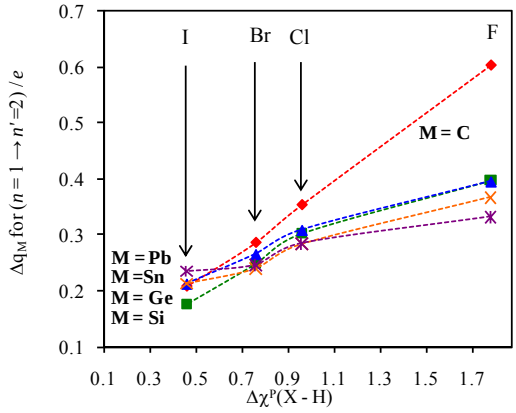


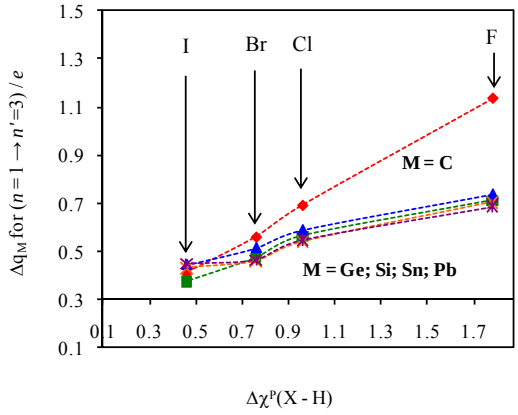


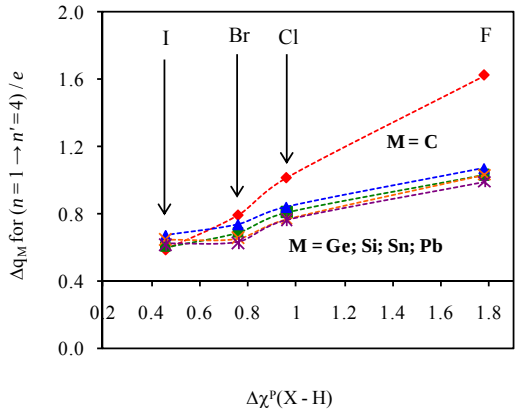


Δn	M	a	b	R^2
1	C	0.619	-0.461	0.999
2	C	1.303	-0.987	1.000
3	C	2.052	-1.577	1.000
1	Si	0.143	-0.101	0.967
2	Si	0.278	-0.205	0.949
3	Si	0.429	-0.329	0.936
1	Ge	0.224	-0.082	0.988
2	Ge	0.458	-0.185	0.984
3	Ge	0.742	-0.339	0.984

MP2 (APT) Basis Set: 6-311+G*

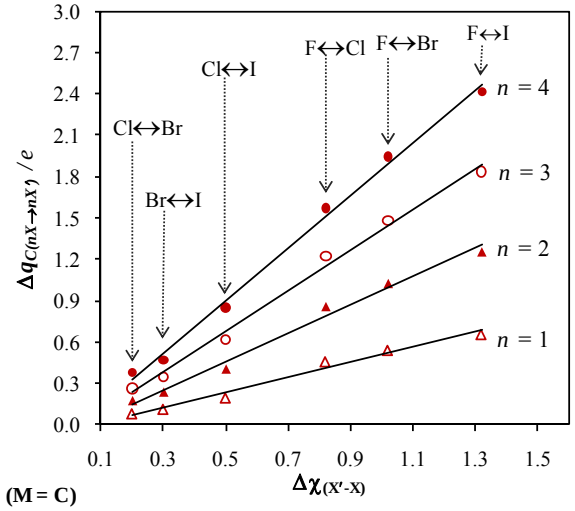






Δn	M	a	b	R^2	M	a	b	R^2
1	C	0.303	0.062	0.999	Sn	0.118	0.158	0.985
2	C	0.552	0.154	0.999	Sn	0.213	0.322	0.979
3	C	0.790	0.223	0.997	Sn	0.310	0.467	0.959
1	Si	0.161	0.122	0.953	Pb	0.076	0.200	0.953
2	Si	0.247	0.288	0.959	Pb	0.189	0.350	0.965
3	Si	0.329	0.456	0.983	Pb	0.300	0.451	0.957
1	Ge	0.135	0.162	0.974				
2	Ge	0.223	0.351	0.983				
3	Ge	0.310	0.520	0.990				

Sample plots of the equation ($[q_{M(n')} - q_{M(n)}] = a[\chi_{A'} - \chi_A] + b$), for A = X. See caption on next page.



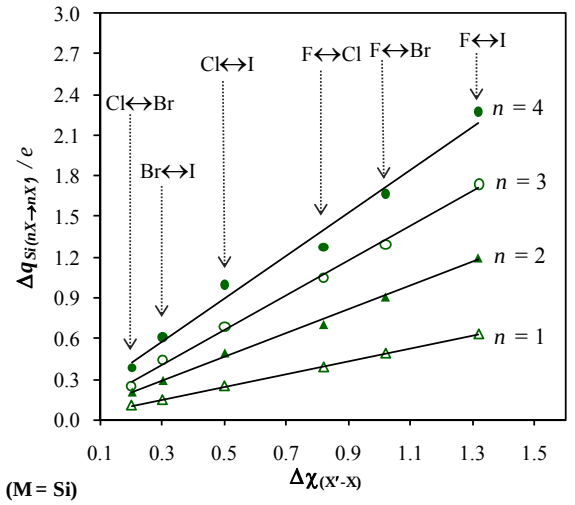
y = 1.908x - 0.050
R² = 0.996

y = 1.474x - 0.061
R² = 0.993

y = 1.029x - 0.058
R² = 0.988

y = 0.546x - 0.039
R² = 0.982

(M = C)



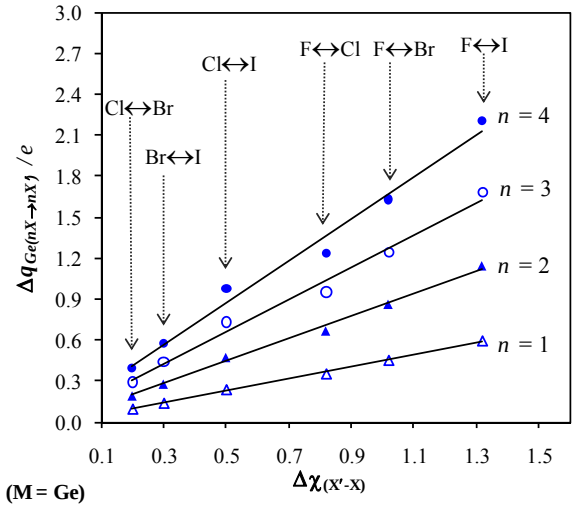
y = 1.585x + 0.103
R² = 0.985

y = 1.277x + 0.025
R² = 0.997

y = 0.869x + 0.030
R² = 0.996

y = 0.475x + 0.005
R² = 1.000

(M = Si)



y = 1.535x + 0.105
R² = 0.984

y = 1.179x + 0.071
R² = 0.987

y = 0.826x + 0.032
R² = 0.995

y = 0.435x + 0.011
R² = 0.998

(M = Ge)

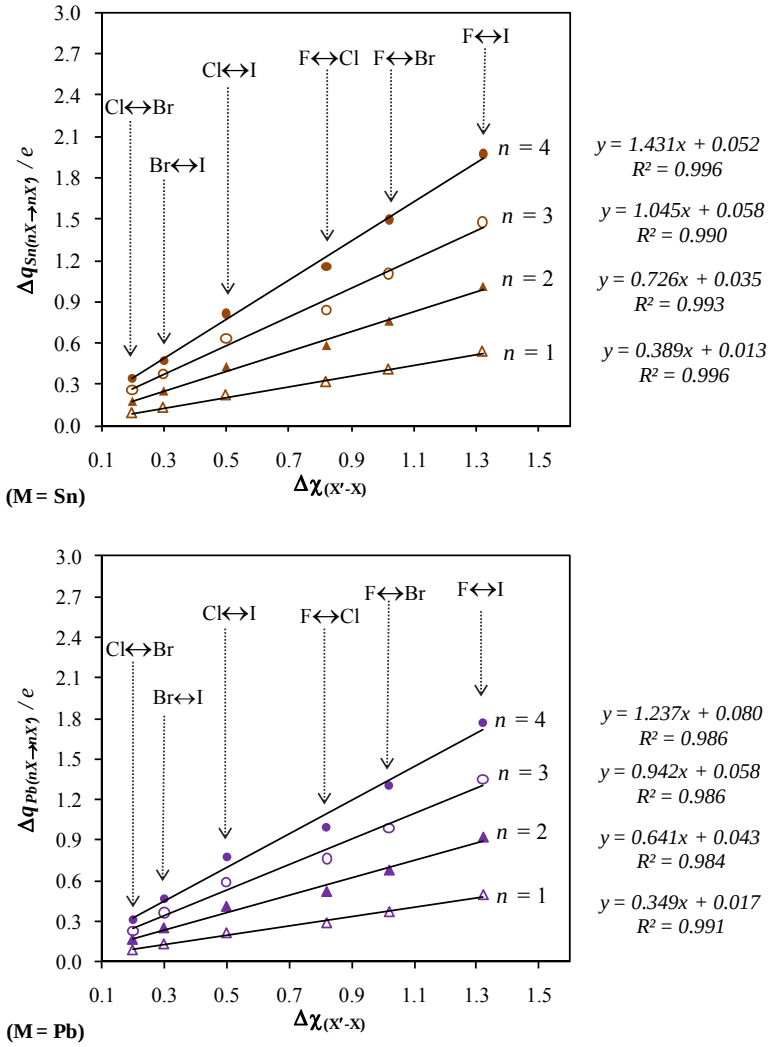
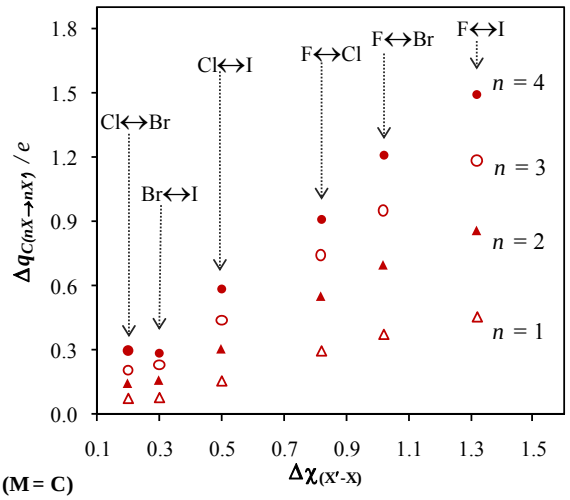


Figure S.6: *$\Delta q_{M(nX\rightarrow nX')}$ vs. $\Delta\chi_{(X'-X)}$ going from $MH_{4-n}X_n$ to $MH_{4-n}X'_n$ for M = C, Ge, and Pb for the CCSD/aug-cc-pVTZ (NBO) q_M data (M = Si, and Sn are included in the supporting information).*



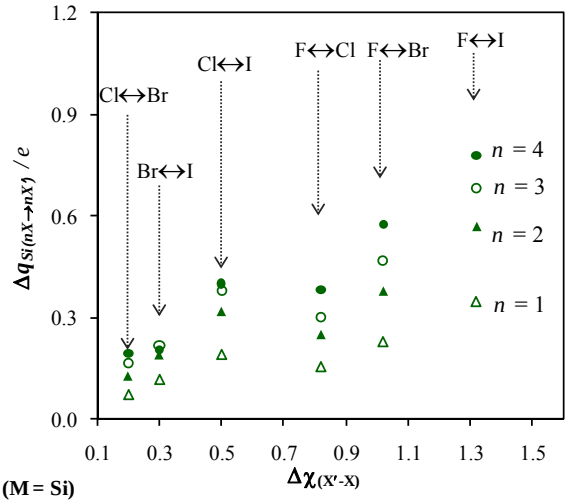
(M = C)

y = 1.128x + 0.015
R² = 0.991

y = 0.914x - 0.006
R² = 0.996

y = 0.673x - 0.014
R² = 0.994

y = 0.366x - 0.011
R² = 0.991



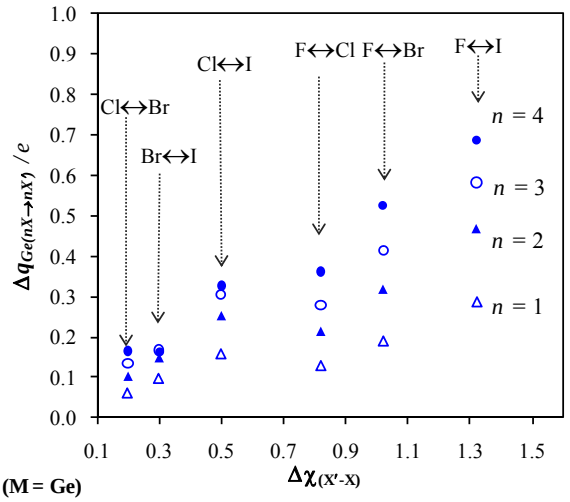
(M = Si)

y = 0.495x + 0.079
R² = 0.924

y = 0.399x + 0.093
R² = 0.849

y = 0.328x + 0.078
R² = 0.836

y = 0.203x + 0.046
R² = 0.845



(M = Ge)

y = 0.463x + 0.050
R² = 0.959

y = 0.362x + 0.063
R² = 0.910

y = 0.280x + 0.058
R² = 0.873

y = 0.167x + 0.037
R² = 0.847

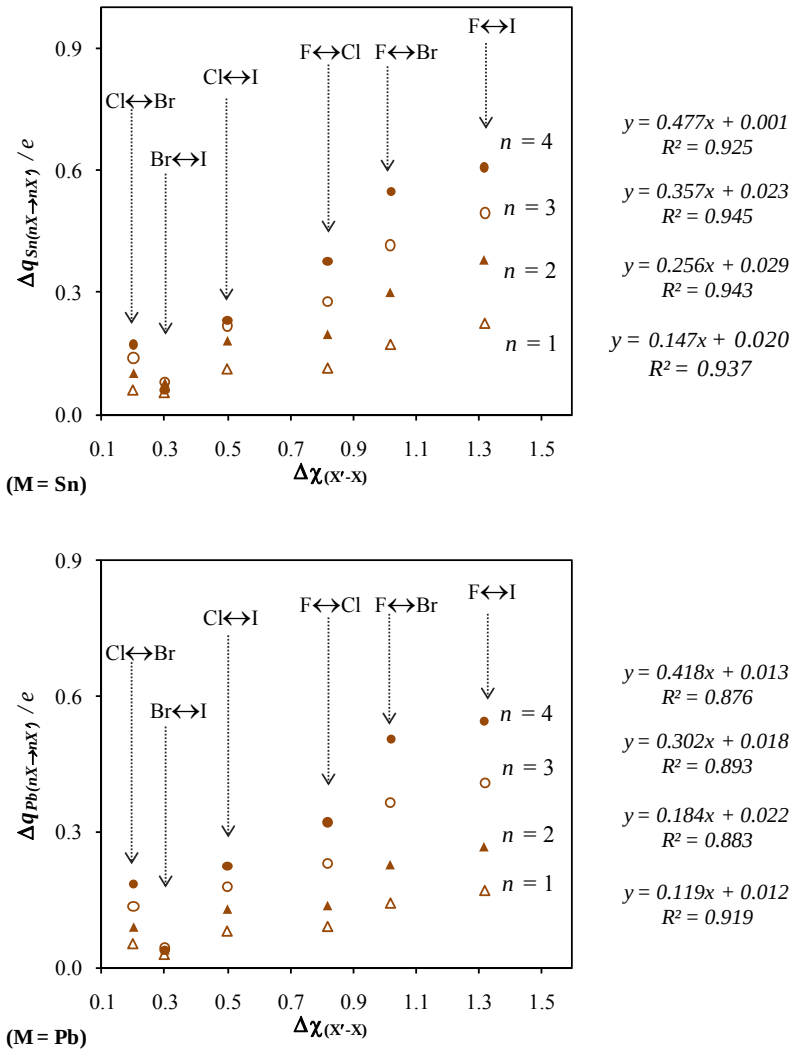


Figure S.7: *$\Delta q_{M(nX\rightarrow nX')}$ vs. $\Delta\chi_{(X'-X)}$ going from $MH_{4-n}X_n$ to $MH_{4-n}X'_n$ for M = C, Ge, and Pb for the MP2(full)/6-311+G* (APT) q_M data (M = Si, and Sn are included in the supporting information).*

NOTE: The linear trends are observed for the NBO data, but they are unreliable for the APT values. A linear dependence is evident for M = C above, but the situation deteriorates thereafter: (we have excluded the best fit lines to allow for careful examination of the more scattered APT values. The Br→I data points are particularly low for M = Sn and Pb (relative to the rest of the values) due to the similarity of APT q_M values for X = Br and I for each *n*. We do not consider the AIM data here since we have been able to include the iodides in our AIM calculations.

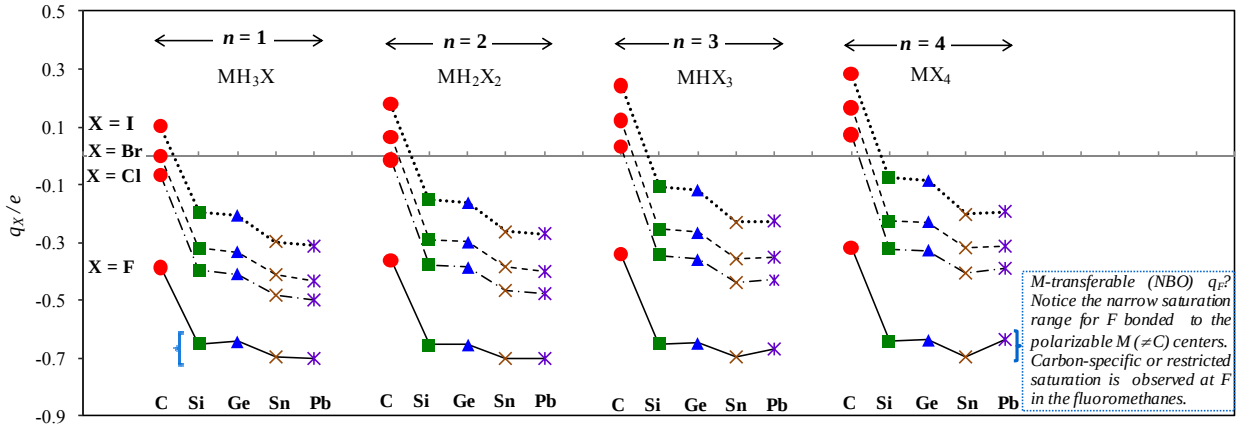


Figure S.8a: *NBO point charges obtained at the CCSD level of theory for the halides, q_X. For the elements preceding Sn in the periodic table, the aug-cc-pVTZ basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

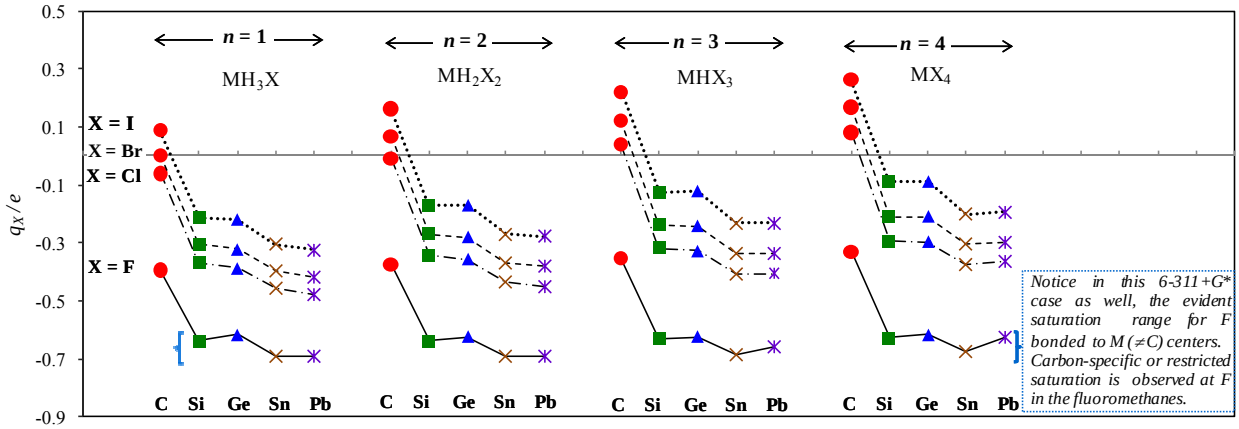


Figure S.9b: *NBO point charges obtained at the CCSD level of theory for the halides, q_X. For the elements preceding Sn in the periodic table, the 6-311+G* basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section. The differences in the data for the two basis sets (cf. Figure S.6a above) are hardly perceptible.*

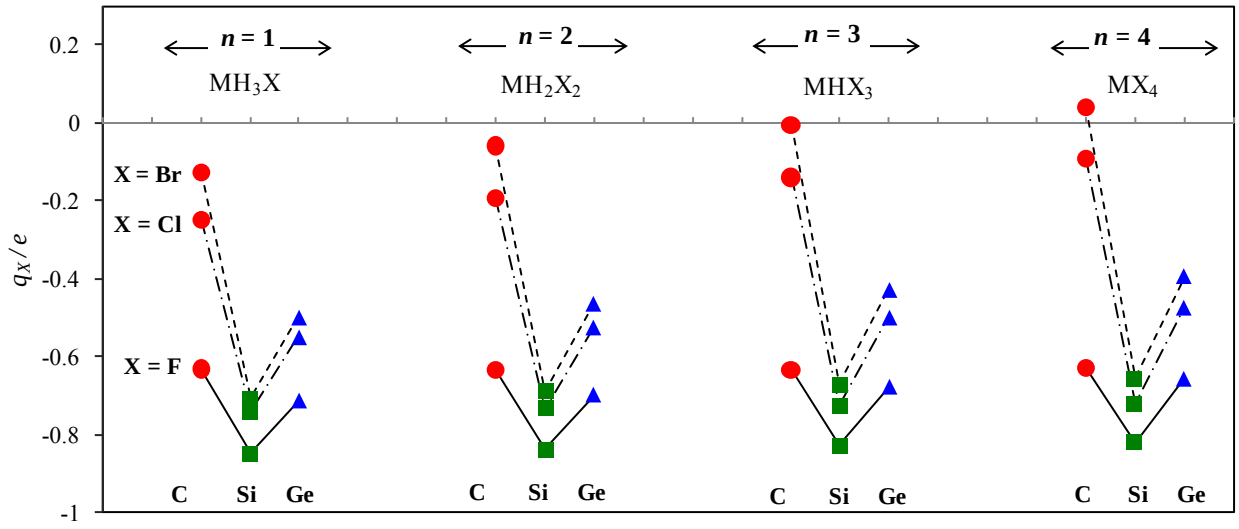


Figure S.10: *AIM point charges obtained at the MP2(full) level of theory for the halides, q_X. For the elements preceding Sn in the periodic table, the 6-311+G* basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*

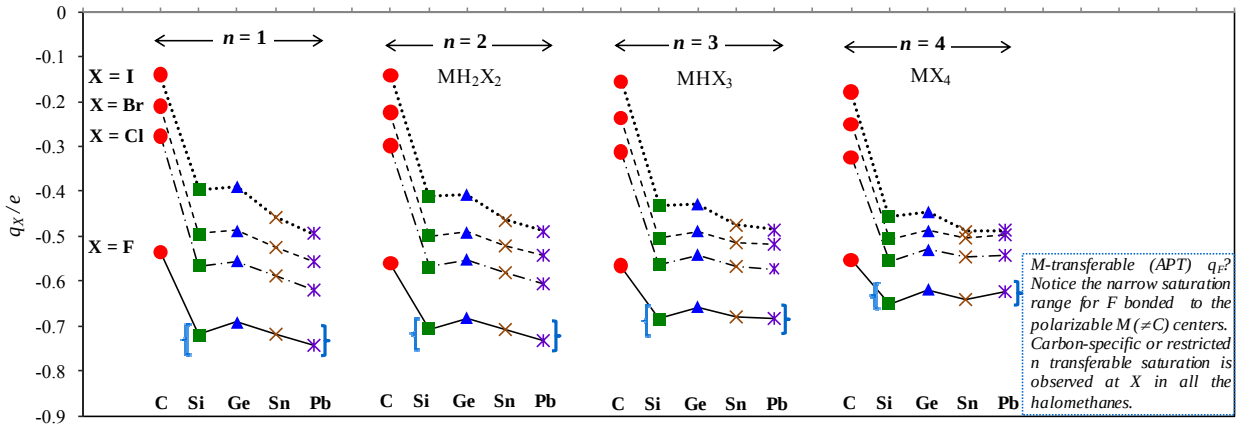


Figure S.11: *APT point charges obtained at the MP2(full) level of theory for the halides, q_X. For the elements preceding Sn in the periodic table, the 6-311+G* basis sets were used. For the heavier elements, the basis sets and ECPs are given in the methods section.*