Multidimensional Lewis Acidity: A Consistent Data Set of Chloride, Hydride, Methide, Water and Ammonia Affinities for 183 p-Block Element Lewis Acids
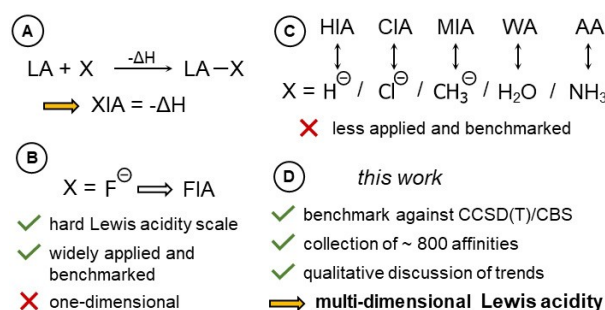
Philipp Erdmann[a] and Lutz Greb*[a]

The computed fluoride ion affinity (FIA) is a widely applied descriptor to gauge Lewis acidity. Like every other single-parameter Lewis acidity scale, the FIA metric suffers from the one-dimensionality, that prohibits addressing Lewis acidity by the multidimensionality it inherently requires (i.e., reference Lewis base dependency). However, a systematic screening of computed affinities other than the FIA is much less developed. Herein, we extended our CCSD(T)/CBS benchmark of different density functionals and the DLPNO-CCSD(T) method for chloride (CIA), methide (MIA), hydride (HIA), water (WA), and ammonia (AA) affinities. The best performing methods are subsequently applied to yield nearly 800 affinities for 183 p-block element compounds of group 13–16 with an estimated accuracy of $< 10\ kJ\,mol^{-1}$. The study's output serves as a consistent library for qualitative analyses and a training set for future statistical approaches. A first holistic correlation analysis underscores the need for a multidimensional description of Lewis acidity.

1. Introduction

As a steadily developing field of interest, Lewis acids exhibit an astonishing number of applications in multiple areas of chemistry.[1] Since G. N. Lewis qualitatively defined Lewis acids as electron-pair acceptors and Lewis bases as electron-pair donors,[2] many metrics have been perceived to order and explain the meaning of Lewis pair formation and Lewis acidity.[3] Nowadays, most experimental scales are based on the spectroscopic changes of a probe Lewis base upon forming an adduct to a Lewis acid (*effective scales*).[4] At the same time, most theoretical methods compute the thermodynamic parameters (ΔH, ΔG, *global scales*) of adduct formation. As an alternative, Lewis acid's intrinsic properties can be considered without a Lewis base perturbation to a limited extent (*e.g.*, LUMO energy, global electrophilicity index, *intrinsic scales*).[5] However, every scale has its limitation, mainly caused by the inevitable restriction to the reference Lewis base, and it is most meaningful to treat Lewis acidity as a multidimensional phenomenon.[6] Although strategies to mitigate Lewis base dependencies have been proposed, and an empirical explanation was offered by Pearson's model of hard and soft acids and bases (HSAB), a *unified* Lewis acidity scale remains questionable, given the multitude of variables and the weight-ing of these variables for the specific problem of interest.[6a,7] Hence, rather than attempting to condense Lewis acidity on a single parameter, it is more the quantity of data that promises to tackle Lewis acidity with the flexibility it demands.[8] Modern quantum chemical computations matured to produce highly accurate adduct formation enthalpies, even for difficult cases and highly decorated but synthetically relevant Lewis acids.[9] Such affinities (XIA) represent the negative enthalpy of the reaction of Lewis acids and a probe Lewis base X, conventionally in vacuum (Figure 1A). The predominantly applied fluoride ion affinity (FIA)[10] is considered to reflect the *hard* Lewis acid character according to the HSAB principle and served to define Lewis superacids (Figure 1B).[11] The calculation of FIA has been systematically benchmarked and applied.[10b–d,12] Nevertheless, the FIA remains a one-dimensional metric, and the transfer to evaluate the respective Lewis acid for applications with different "demands" can lead to misinterpretation. Other ion affinity scales, such as hydride (HIA),[12a,13] chloride (CIA)[13d,14] and methide (MIA)[13d,14a,15] ion affinities were also used to gauge varying Lewis acid characteristics (Figure 1C). Beyond the anion

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Figure 1. A–C Previously applied Lewis base affinities (XIA) and **D** its shortcomings considered in this work.

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affinities, also ammonia affinity (AA)[13c,14a,c,16] and water affinity (WA)[14a] have been computed. However, the limited number of values available in the literature suffer from similar issues as reported for the FIA: comparability (*e.g.*, different theory levels) and reliability (quality of the used level of theory).

In the present work, we put the HIA, CIA, MIA, WA, and AA on the same level as we did for the FIA (Figure 1D).[12c] In the first part, the DLPNO-CCSD(T) method and selected density functionals are benchmarked against canonical CCSD(T)/CBS values. The second part provides the data, and a brief discussion of the respective affinity of 183 literature-known and hypothetical *p*-block element Lewis acids under vacuum and solvation corrected conditions. It is intended as a *de novo* database in addition to our FIA calculations for a further theoretical and practical discussion on the topic of Lewis acidity to come. Hydride, being regarded as an easily polarizable Lewis base, should project information in the domain of *soft* interactions while keeping steric repulsion and π-bonding effects absent. On the opposite, beneath their varying HSAB character, chloride and methide affinities transport information on steric contributions to Lewis acidity. Ammonia and water as weaker donors reflect the domain of less stable Lewis adducts, whose formation enthalpies may be governed by additional Lewis acid properties (such as dispersion, H-bonding), less critical for the stronger adducts.[17] Overall, the broad assessment of a variety of Lewis acid – Lewis base pair formation enthalpies ideally prepares for a statistical treatment, which profits from a massive amount of reliable and comparable data.

Methods

Structure optimization of all compounds was carried out at the threefold-corrected PBEh-3c/def2-mSVP level of theory by basis which includes geometrical counterpoise correction to remove artificial overbinding effects by basis set superposition error (BSSE).[18] The accuracy of this composite method is comparable to triple-ζ basis set second-order perturbation theory (MP2/TZ) throughout the periodic table.[18] A small geometric benchmark against experimental data for neutral and anionic species confirmed the suitability (see supporting information, Table S1). VSEPR and non-VSEPR structures were applied as starting geometries, and all final structures were verified to be local minima by frequency analysis. Zero-point energies and thermal corrections as implemented in ORCA 4.2.1 were carried over for the single-point computations.[19] It shall be noted that some starting geometries do not result in stable adducts, *e.g.*, a considerable number for water and ammonia adducts, and were eliminated from the data set. A representative set of Lewis acids was selected for a benchmark of adduct formation enthalpies with all considered Lewis bases, and the reference data computed non-isodesmically at coupled-cluster theory with singles and doubles, including perturbative triples correction CCSD(T) (Table 1). Slow basis set conversion of CCSD(T) was treated by a two-point extrapolation scheme to the complete basis set (CBS) with aug-cc-pVnZ (n=3,4) using the optimized fitting parameters of Neese and Valeev.[20] Potential errors by missed static electron correlation were excluded from T1-diagnostics and fractional occupation number weighted electron density (FOD) calculations.[21] The calculated benchmark affinities correspond well with previous calculations on comparable coupled-cluster levels of theory.[13d,22] Against the limited number of experimentally determined values, the herby computed HIA are in good agreement.[23] For the isodesmic anchoring at the lower level methods, the affinities for the Me_3Si^+ were recomputed at the same CCSD(T)/CBS level.[13d]

Subsequently, selected density functionals and DLPNO/CCSD(T) methods at different thresholds of coupled pair truncation were considered for computing the benchmark enthalpy set.[24] The XIA-values were calculated with and without isodesmic anchoring to the CCSD(T)/CBS values of the trimethylsilylium (TMS) system. Non-isodesmic computation corresponds to the calculation of the bare reaction enthalpy $LA + X \rightarrow LA–X$, whereas isodesmic means computing $LA + TMS–X \rightarrow LA–X + TMS^+$ and subtracting the CCSD(T)/CBS value of $TMS–X \rightarrow TMS^+ + X$. Generally, isodesmic computation is meant to improve the absolute affinities for cases in which the proper description of "naked" X is feasible only at a highly correlated level of theory. Interestingly, the reliability of anion affinities (HIA, CIA, MIA) improves by isodesmic anchoring, while the computation of neutral Lewis bases' affinities (WA, AA) should be performed non-isodesmically (see Table S8). The best-performing methods and the respective MAD (mean average deviation) and

Table 1. CCSD(T)/CBS benchmark values in kJ mol^{-1} after two-point extrapolation (aug-cc-pVnZ, n=3,4). All numbers are based on non-isodesmic adduct formation reaction. [a] Highest available ab initio level: DLPNO-CCSD(T) aug-cc-pVQZ nPNO. [b] No stable adduct available. "ax"/"eq" = Lewis base in axial/equatorial position (see Figure S1).

	HIA	CIA	MIA	WA	AA
TMS+	924	745	981	152	223
BH$_3$	305	143	342	47	116
BF$_3$	296	146	356	30	84
BCl$_3$	405	196	462	25	105
BBr$_3$	437	218	499	33	121
B(C$_6$F$_5$)$_3$[a]	481	257	502	55	112
AlF$_3$	401	308	454	123	164
AlCl$_3$	435	323	492	113	157
GaF$_3$	460	318	511	114	166
SiF$_{4,"ax"}$	254	111	304	12	33
SiCl$_{4,"ax"}$	300	109	351	0	6
GeF$_{4,"ax"}$	358	187	412	31	74
SiF$_{4,"eq"}$	269	103	320	–[b]	–[b]
SiCl$_{4,"eq"}$	318	–[b]	371	–[b]	–[b]
GeF$_{4,"eq"}$	379	185	431	–[b]	–[b]
PF$_5$	404	163	437	23	89
AsF$_5$	483	245	533	60	131
SbF$_5$	533	326	585	96	159

Table 2. Performance of the best density functional and ab initio method as "level of choice" for the respective affinity. HIA, CIA and MIA with isodesmic anchoring to the TMS-reference system, WA and AA, non-isodesmic computation. L1 = DLPNO-CCSD(T)/aug-cc-pVQZ, L2a = DSD-PBEP86-D3BJ/def2-QZVPP, L2b = DSD-BLYP–D3BJ/def2-QZVPP. Values in kJ mol^{-1}.

	HIA		CIA		MIA		WA		AA	
	L1	L2a	L1	L2a	L1	L2a	L1	L2a	L1	L2a
MAD	1.4	2.0	1.8	1.6	1.7	3.1	1.4	2.2	1.4	3.5
RMSD	1.7	2.8	2.1	2.1	3.3	5.0	1.7	2.9	1.8	5.5

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RMSD (root means square deviation) against the CCSD(T)/CBS values can be found in Table 2 (further details see Table S3–S8).

DLPNO-CCSD(T) at normal coupled pair truncation level (normal-PNO) with the aug-cc-pVQZ basis set was identified as the most suitable method and applied whenever allowed by the size of the system (denoted: standard model *L1*). The DSD-PBEP86-D3(BJ)/def2-QZVPP density functional turned out as the second-most accurate model, whereas the DSD-BLYP−D3(BJ)/def2-QZVPP model was used for systems containing aromatic ring systems (better performance with $B(C_6F_5)_3$ in benchmark).[25] Hence, those two double-hybrid models were used for the larger Lewis acids, denoted as standard model *L2a* (DSD-PBEP86) and *L2b* (DSD-BLYP). The basis set superposition error (BSSE) for the double-hybrid models was considered by counterpoise correction using the procedure of Boys and Bernardi (see Table S2).[26] It does not improve performance, and all XIAs are presented without BSSE correction.

Cases for which both ab initio values (*L1*) and DFT results (*L2*) were available, a matching within chemical accuracy gave further confidence for the chosen methods' general accuracy and robustness (see Table S9). All anionic Lewis base affinities were computed with TMS anchoring but non-isodesmically (conventionally) for the neutral Lewis base affinities.

Solvation corrected affinities (denoted as XIA_{solv}) were obtained with COSMO-RS[27] in dichloromethane, as implemented in the ADF[28] quantum chemistry package, by computing the solvation energies of the isolated Lewis acids and Lewis bases and the respective adducts:

$$XIA_{solv} = XIA - [\Delta E_{solv}(LA - X) - \Delta E_{solv}(LA) - \Delta E_{solv}(X)]$$

Overall, the applied computational models warrant an estimated accuracy of $<3\ kJ\,mol^{-1}$ for L1-values and $<7\ kJ\,mol^{-1}$ for L2-values and were chosen for the set of 183 literature-known and hypothetical Lewis acids p-block Lewis acids in the highest oxidation states (Table 3) and lower oxidation states (Table 4).

2. Results and Discussion

Plotting the affinities for two different Lewis bases gave, depending on the combination, from good to relatively low correlations (Figure 2 and Table 5). Notably, plotting HIA against MIA, the correlation is quite good, while plotting HIA against the FIA shows signs of diffuseness (Figure 2A). The CIA's plots against the HIA and MIA are even more diffusive and correlate in similar quality with the non-anionic AA (Figure 2B). Plots of WA against AA indicate a reasonable linear correlation, while plots of, *e.g.*, HIA against WA appear virtually uncorrelated (Figure 2C). Hence, it can be stated that there is a gap between the FIA/HIA/MIA at the one hand and WA/AA at the other hand, that is bridged by the CIA. This analysis emphasizes at a glance the dependency of Lewis acidity on the reference Lewis base and the need to scale Lewis acidity (by definition, a thermodynamic value) by more than a single parameter. However, the overall trends indicate that a manageable number of terms should suffice to parametrize Lewis acidity up to a certain amount of validity.

Although the fluoride is considered the classical hard base and the hydride as the classical soft base, the uniform trends indicate that hardness and softness do not oppose each other. Instead, differences become more pronounced if the absolute affinity is lowered. For group 14, group 15 in oxidation state +III, and group 16 Lewis acids, the differences of affinities of axial vs. equatorial Lewis base binding were evaluated by comparing the corresponding values (cf. tables 3/4, equatorial vs. axial binding, for pictorial representation of binding modes, see Figure S1). The mean absolute differences for the two stereoisomeric binding modes among all affinities (Table S10) vary from large (group 15, +III, 51 kJ mol^{-1}/group 16, 46 kJ mol^{-1}) to modest (group 14, 16 kJ mol^{-1}), but cannot be easily generalized by apicophilicity trends or Bent's rule.[29]

Figure 3 holds exemplary information about affinity trends of group 13–15 elements in their highest oxidation state. The MIA dependence for varying halide ligands (Figure 3A) shows similar behavior as in the FIA case, which counts as well for HIA and less pronounced for the CIA (see Figure S2). The lighter central atoms (B, Al, P, Si) experience an increasing affinity along with F < Cl < Br < I, whereas the heaviest central elements (Sn, Sb) show the inverse trend. For the intermediate cases (Ga, As, Ge), only a moderate effect is observed. Interestingly, these trends are different for the AA (Figure 3B) and the WA (Figure S2). Except for boron, the affinities against the neutral
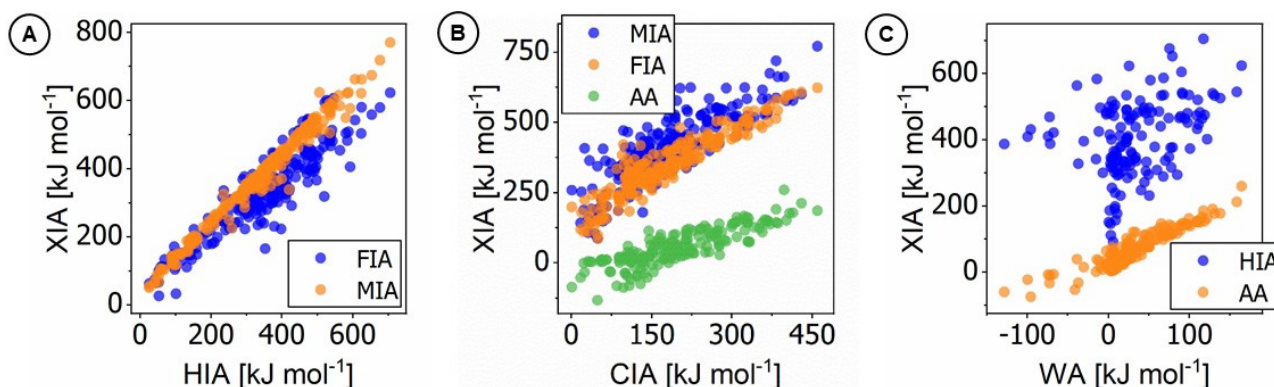
Figure 2. A Correlation plots comparing HIA with MIA and FIA, **B** CIA with MIA, FIA and AA and **C** WA with HIA and AA.

Table 3. Collection of computed HIA, CIA, MIA, WA and AA for group 13–15 element compounds in their highest oxidation states and the respective solvation corrected values (XIA$_{solv}$) in dichloromethane (COSMO-RS). Italic numbers were obtained by the L2a standard model. [a] Computed with the L2b standard model. Empty cells = no stable adduct.

Compound	HIA	HIA$_{solv}$	CIA	CIA$_{solv}$	MIA	MIA$_{solv}$	WA	WA$_{solv}$	AA	AA$_{solv}$
BBr$_3$	439	437	220	133	497	421	34	51	121	149
B(C$_2$F$_5$)$_3$	624	589	397	281	662	552	164	175	260	277
B(C$_6$F$_5$)$_3$	*484*	416	*254*	110	*506*	361	*54*[a]	57	*122*[a]	134
B(CCH)$_3$	364	378	167	99	408	344	28	41	101	125
BCl$_3$	403	411	194	115	457	391	22	41	102	133
BF$_3$	297	343	146	94	354	320	29	45	83	115
BH$_3$	305	367	144	107	340	317	46	65	114	145
BI$_3$	473	455	243	141	525	433	31	46	122	147
B(Me)$_3$	240	254	105	35	292	216	8	13	60	74
B(N(C$_6$F$_5$)$_2$)$_3$	*386*	293	*118*	−51	*365*	197			*−14*[a]	−11
B(NH$_2$)$_3$	88	116	17	−29	143	84			−53	−48
B(OC$_6$F$_5$)$_3$	393	326	198	49	422	305	21	22	65	76
B(OC(CF$_3$)$_3$)$_3$	410	354	206	64	443	306	24	21	44	56
B(OH)$_3$	140	188	37	−14	192	156			4	6
B(Ph)$_3$	*329*	299	*154*	46	*368*	258	*3*[a]	5	*56*[a]	69
B(SH)$_3$	320	320	125	39	372	295			35	58
AlBr$_3$	447	425	331	226	506	412	111	126	157	179
Al(C$_2$F$_5$)$_3$	545	492	430	294	601	472	158	162	212	220
Al(C$_6$F$_5$)$_3$	476	402	361	210	528	376	119	122	154	164
Al(CCH)$_3$	373	371	276	191	424	345	101	110	139	157
AlCl$_3$	433	423	321	224	488	400	110	124	154	177
AlF$_3$	402	411	309	226	452	386	122	136	162	184
AlH$_3$	317	326	227	152	360	296	77	90	114	135
AlI$_3$	452	418	328	213	509	403	98	109	144	164
Al(Me)$_3$	290	284	215	126	338	249	68	74	99	111
Al(N(C$_6$F$_5$)$_2$)$_3$	*471*	374	*342*	166	*519*	345	*89*[a]	90	*127*[a]	133
Al(NH$_2$)$_3$	232	247	159	87	280	214	50	47	77	85
Al(OC$_6$F$_5$)$_3$	*483*	403	*366*	209	*537*	383	*113*[a]	119	*151*[a]	166
Al(OC(CF$_3$)$_3$)$_3$	473	407	365	219	529	386	109	118	152	165
Al(OH)$_3$	294	313	215	145	343	286	85	90	117	131
Al(Ph)$_3$	*349*	312	*257*	142	*398*	281	*75*[a]	78	*109*[a]	119
Al(SH)$_3$	377	358	273	169	429	335	79	86	115	131
GaBr$_3$	466	452	304	203	521	433	88	99	141	163
Ga(C$_2$F$_5$)$_3$	541	493	382	254	587	464	128	132	191	201
Ga(C$_6$F$_5$)$_3$	*480*	407	*329*	182	*524*	373	*97*[a]	101	*143*[a]	154
Ga(CCH)$_3$	376	377	240	160	420	347	77	84	119	138
GaCl$_3$	464	454	307	212	516	437	94	106	146	170
GaF$_3$	464	478	322	244	510	453	116	130	167	194
GaH$_3$	309	330	190	125	345	291	60	69	99	118
GaI$_3$	466	436	299	189	519	418	74	83	128	147
Ga(Me)$_3$	272	271	174	92	313	230	44	48	75	87
Ga(N(C$_6$F$_5$)$_2$)$_3$	*480*	392	*309*	145	*523*	360	*46*[a]	57	*92*[a]	109
Ga(NH$_2$)$_3$	248	261	148	75	292	225	40	37	64	71
Ga(OC$_6$F$_5$)$_3$	542	462	356	203	583	433	91	95	142	157
Ga(OC(CF$_3$)$_3$)$_3$	538	472	368	221	584	442	92	99	149	165
Ga(OH)$_3$	338	352	214	143	384	325	70	75	108	124
Ga(Ph)$_3$	*333*	299	*213*	104	*373*	259	*47*[a]	49	*80*[a]	89
Ga(SH)$_3$	379	364	238	139	428	340	57	61	97	111
axial Lewis base binding in group 14										
SiBr$_4$	327	308	125	26	378	288	6	6	13	29
Si(C$_2$F$_5$)$_4$			205	79	422	302	−4	0	24	35
Si(C$_6$F$_5$)$_4$	*236*	156	*125*	−30	*327*	170				
Si(CCH)$_4$	191	198	64	−7	245	172	8	4	11	12
SiCl$_4$	300	291	107	15	357	276	−7	0	7	23
SiF$_4$	254	281	110	45	302	252	4	14	34	55
SiH$_4$	92	120	35	−16	144	89	6	7	5	5
SiI$_4$	342	309	134	23			4	−1	7	14
Si(Me)$_4$	68	62	43	0	104	13				
Si(N(C$_6$F$_5$)$_2$)$_4$			97	−88	471	314			*−88*[a]	−90
Si(NH$_2$)$_4$	96	116			137	72				
Si(OC$_6$F$_5$)$_4$	*401*	361	*226*	64			*3.5*[a]	6.1	*55*[a]	60
Si(OC(CF$_3$)$_3$)$_4$	*342*	268	*104*	−51	*334*	185			*−45*	−41
Si(OH)$_4$	152	176	133	54	180	130				
Si(Ph)$_4$	*160*	119	*48*	−56	*190*	71				
Si(SH)$_4$	286	270	129	26	328	240			10	17
GeBr$_4$	354	333	146	45	410	318	10	10	22	33
Ge(C$_2$F$_5$)$_4$	360	313	172	47	380	257			13	17
Ge(C$_6$F$_5$)$_4$	*278*	196	*118*	−34	*311*	154				

Table 3. continued										
Compound	HIA	HIA$_{solv}$	CIA	CIA$_{solv}$	MIA	MIA$_{solv}$	WA	WA$_{solv}$	AA	AA$_{solv}$
Ge(CCH)$_4$	177	181	56	−14	228	154	11	10	11	13
GeCl$_4$	350	338	147	52	401	319	6	5	26	36
GeF$_4$	358	377	185	111	406	353	29	35	72	60
GeH$_4$	59	81	31	−11	108	48	6	11	5	5
GeI$_4$	346	310	135	22	399	291	3	1	4	54
Ge(Me)$_4$	53	45	49	3	88	−5				
Ge(N(C$_6$F$_5$)$_2$)$_4$			142	−44	483	324	−41^a	−46	−52^a	−55
Ge(NH$_2$)$_4$	137	150	87	24	186	113				
Ge(OC$_6$F$_5$)$_4$			276	115	520	364	20^a	24	60^a	75
Ge(OC(CF$_3$)$_3$)$_4$	445	371	181	26	462	313			0	47
Ge(OH)$_4$	216	236	151	67	268	209			38	43
Ge(Ph)$_4$			50	−48	168	47				
Ge(SH)$_4$	293	272	137	34	337	244	11	7	20	23
SnBr$_4$	380	351	197	87	434	335	15	17	47	60
Sn(C$_2$F$_5$)$_4$	379	329	228	100	421	295	16	17	36	42
Sn(C$_6$F$_5$)$_4$	334	251	192	38	378	220	19^a	18	29^a	33
Sn(CCH)$_4$	232	227	108	29	278	197	15	14	26	31
SnCl$_4$	393	371	211	106	435	345	22	26	57	72
SnF$_4$	440	445	269	182	484	420	64	73	110	131
SnH$_4$	111	120	53	−10	152	83	3	6	5	8
SnI$_4$	366	324	183	65	420	307	7	7	31	39
Sn(Me)$_4$	112	96	59	−19	149	51			5	4
Sn(N(C$_6$F$_5$)$_2$)$_4$			250	66	475	295	4^a	2	38^a	39
Sn(NH$_2$)$_4$	210	209	123	39	254	172				
Sn(OC$_6$F$_5$)$_4$			352	189			57^a	64	123^a	137
Sn(OC(CF$_3$)$_3$)$_4$	518	442	286	129	541	393	39	40	81	89
Sn(OH)$_4$	294	302	188	97	328	264	49	45	76	83
Sn(Ph)$_4$	209	164	108	−4	233	109			14^a	11
Sn(SH)$_4$	320	293	183	72	364	266	21	17	40	47
equatorial Lewis base binding in group 14										
SiBr$_4$	344	328	126	27	399	313				
Si(C$_2$F$_5$)$_4$	409	362			425	304				
Si(C$_6$F$_5$)$_4$	339	257	108	−53	359	202			−80^a	−70
Si(CCH)$_4$	210	214	39	−39	264	193				
SiCl$_4$	317	311	107	15	368	291				
SiF$_4$	270	299	103	39	318	273				
SiH$_4$	92	120			142	92				
SiI$_4$	359	329	135	23	414	314				
Si(Me)$_4$	63	53			104	13				
Si(N(C$_6$F$_5$)$_2$)$_4$	432	326	129	−58			−96^a	−100	−74^a	−74
Si(NH$_2$)$_4$	89	101			134	65				
Si(OC$_6$F$_5$)$_4$	413	327	217	95	459	299			32^a	43
Si(OC(CF$_3$)$_3$)$_4$	368	293	95	−60	350	201				
Si(OH)$_4$	144	168			194	140				
Si(Ph)$_4$	161	117			197	74				
Si(SH)$_4$	290	268	100	−4	340	246			−35	−20
GeBr$_4$	376	358	144	41	433	347				
Ge(C$_2$F$_5$)$_4$	368	321			388	268				
Ge(C$_6$F$_5$)$_4$	326	242	107	−53	351	194				
Ge(CCH)$_4$	203	204	19	−59	253	182				
GeCl$_4$	372	364	147	52	425	349				
GeF$_4$	377	400	184	112	426	379				
GeH$_4$	59	81			104	51				
GeI$_4$	368	337	131	16	421	320				
Ge(Me)$_4$	47	34			88	−5				
Ge(N(C$_6$F$_5$)$_2$)$_4$	469	363	153	−33			−73^a	−77	−33^a	−35
Ge(NH$_2$)$_4$	142	145			182	109				
Ge(OC$_6$F$_5$)$_4$	488	408	276	113	548	391			64^a	76
Ge(OC(CF$_3$)$_3$)$_4$	476	400			480	332				
Ge(OH)$_4$	240	255			299	234				
Ge(Ph)$_4$	145	100			179	54				
Ge(SH)$_4$	306	283	104	−2	356	261				
SnBr$_4$	395	369	196	85	450	356				
Sn(C$_2$F$_5$)$_4$	404	353	210	82	447	323				
Sn(C$_6$F$_5$)$_4$	367	282	169	10	407	248				
Sn(CCH)$_4$	251	245	88	4	297	220				
SnCl$_4$	405	387	211	106	447	362				
SnF$_4$	450	458	272	187	494	435				
SnH$_4$	113	122			150	86				
SnI$_4$	381	343	179	58	434	326				

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Table 3. continued

Compound	HIA	HIA$_{solv}$	CIA	CIA$_{solv}$	MIA	MIA$_{solv}$	WA	WA$_{solv}$	AA	AA$_{solv}$
Sn(Me)$_4$	117	97			149	51				
Sn(N(C$_6$F$_5$)$_2$)$_4$	501	395	277	94	521	342	1[a]	−1	29[a]	30
Sn(NH$_2$)$_4$					254	173				
Sn(OC$_6$F$_5$)$_4$	560	476	357	193	616	459			110[a]	119
Sn(OC(CF$_3$)$_3$)$_4$	537	461			566	417				
Sn(OH)$_4$	312	315			371	298				
Sn(Ph)$_4$	207	158			242	115				
Sn(SH)$_4$	331	305	159	45	379	277				
PBr$_5$	496	472	193	87	528	435	6	4	67	82
P(C$_2$F$_5$)$_5$	580	525	271	135	550	420	52	50	91	99
P(C$_6$F$_5$)$_5$	420	330	85	-81	339	175			-82[a]	-82
P(CCH)$_5$	318	321	105	31	355	282	3	3	38	48
PCl$_5$	477	464	177	79	502	420	-3	-1	64	83
PF$_5$	406	432	165	97	437	390	23	34	89	118
PH$_5$	152	177	55	1	204	148	1	1	9	12
PI$_5$	483	444	182	62	517	407	-3	-7	37	46
P(Me)$_5$	136	117	31	−27	156	57				
P(NH$_2$)$_5$	97	100			117	39			−92	−96
P(OC$_6$F$_5$)$_5$	505	416	223	56	624	517	8[a]	9	50[a]	61
P(OC(CF$_3$)$_3$)$_5$	584	503	203	40	622		−14	−17	38	42
P(OH)$_5$	189	211			220	163				
P(Ph)$_5$	258	204	56	−59	226	95				
P(SH)$_5$	328	300	73	−33	354	253	−37	−43	−32	−27
AsBr$_5$	491	467	215	108	546	453	22	22	78	91
As(C$_2$F$_5$)$_5$	480	423	214	79		345	2	0		39
As(C$_6$F$_5$)$_5$	399	308	123	−43	371	205			−44[a]	−45
As(CCH)$_5$	312	309	116	37	363	286	11	7	41	46
AsCl$_5$	491	477	218	118	538	457	23	26	83	100
AsF$_5$	486	508	249	176	533	486	62	73	132	159
AsH$_5$	146	164	59	0	200	138	3	2	11	12
AsI$_5$	473	433	195	168	518	407	7	52	46	54
As(Me)$_5$	135	114	50	−27	166	63				
As(NH$_2$)$_5$	158	158			191	110				
As(OC$_6$F$_5$)$_5$	587	497	324	156	624	459	68[a]	70	116[a]	127
As(OC(CF$_3$)$_3$)$_5$	624	543	289	126	622	468	25	24	77	83
As(OH)$_5$	268	285	89	15	313	253			22	29
As(Ph)$_5$	251	196	90	−26	250	119			2[a]	−4
As(SH)$_5$	342	311	111	3	386	283	−15	−21	2	3
SbBr$_5$	487	457	260	148	549	450	43	46	93	107
Sb(C$_2$F$_5$)$_5$	483	424	275	138	519	387	36	37	75	84
Sb(C$_6$F$_5$)$_5$	416	323	211	43	441	274	2[a]	-2	26[a]	28
Sb(CCH)$_5$	343	339	167	86	385	307	32	33	68	77
SbCl$_5$	496	475	271	165	553	464	50	56	108	125
SbF$_5$	535	540	328	239	585	523	99	107	163	184
SbH$_5$	199	200	97	22	246	174	8	9	21	25
SbI$_5$	465	422	242	118	524	410	27	27	70	79
Sb(Me)$_5$	187	162	89	−2	226	121	2	0	8	10
Sb(NH$_2$)$_5$	233	221	114	21	268	181			8	8
Sb(OC$_6$F$_5$)$_5$	606	516	385	217	663	499	90[a]	95	141[a]	155
Sb(OC(CF$_3$)$_3$)$_5$	653	575	371	211	674	524	79	83	138	149
Sb(OH)$_5$	336	340	168	85	385	316	34	33	72	81
Sb(Ph)$_5$	285	232	151	31	313	183	23[a]	19	37[a]	37
Sb(SH)$_5$	364	333	178	64	412	310	10	6	41	46

donors drop along with F > Cl > Br > I. Carbon-based ligands (Figure 3C) show a similar trend to that found for fluoride ion affinities.[12c] Increasing the s-orbital character of the ligand-carbon atoms (Me(sp³) < Ph(sp²) < CCH(sp)) leads to increasing group electronegativity, which in turn, increases the XIA.[29a] The decreasing steric effect along those groups might certainly also play a role (Me(sp³) > Ph(sp²) > CCH(sp)).[30] For group 15 carbon-containing Lewis acids, some periodic "break" for C$_6$F$_5$ was found for phosphorus. This can be ascribed to steric effects that become detrimental for the small hexacoordinated phosphorous.

Considering the effect of solvation (CH$_2$Cl$_2$, COSMO-RS) for ionic affinities (HIA, MIA, CIA), similar and additional trends can be found as observed previously.[12c] For the larger Lewis acids, chloride and methide affinities are harshly reduced in intensity because of the more considerable solvation free energy of the respective naked ion, which overcompensates the charged adduct's stabilization. Still, small Lewis acids form anionic adducts with large charge density, and solvation damping is thus less effective. Since the hydride anion is less strongly solvated (at least in the COSMO-RS framework) as methide and chloride, solution-phase HIA damping is less pronounced and even inverted for the small Lewis acids. Oversimplified state-

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Table 4. Collection of computed HIA, CIA, MIA, WA and AA for group 15–16 element compounds in their lower oxidation states, some special Lewis acids and the respective solvation corrected values (XIA$_{solv}$) in dichloromethane (COSMO-RS). Italic numbers were obtained by the L2a standard model. [a] Computed with the L2b standard model.

Compound	HIA	HIA$_{solv}$	CIA	CIA$_{solv}$	MIA	MIA$_{solv}$	WA	WA$_{solv}$	AA	AA$_{solv}$
axial Lewis base binding in group 15 and 16										
S(C$_2$F$_5$)$_4$	352	307	34	−70	364	246				
SF$_4$	397	427	24	−38	408	366			−33	−34
SH$_4$	53	65								
S(OC(CF$_3$)$_3$)$_4$			99	−57						
Se(C$_2$F$_5$)$_4$	378	327	59	−68	406	282				
SeF$_4$	427	445	105	34	466	413			27	39
SeH$_4$	101	111			148	88				
Se(OC(CF$_3$)$_3$)$_4$	*592*	518	*196*	41	*577*	429				
Te(C$_2$F$_5$)$_4$	438	382	185	52	478	349	15	11	40	38
TeF$_4$	412	413	162	78	461	390	14	10	76	82
TeH$_4$	131	133	23	−18	188	119			0	0
Te(OC(CF$_3$)$_3$)$_4$	*564*	487	*257*	101	*585*	435	*−39*	−39	*39*	47
PBr$_3$	343	362	119	29	382	339	11	11	15	21
P(C$_2$F$_5$)$_3$	295	263	103	−1	286	186				
PCl$_3$	302	323	100	15	339	295	7	8	10	16
PF$_3$	158	190	65	7	201	153	9	10	12	16
PH$_3$	26	51			51	−7				
P(OC(CF$_3$)$_3$)$_3$	316	260	110	−22	344	220	6	5		
AsBr$_3$	336	346	145	50	376	320	19	20	23	31
As(C$_2$F$_5$)$_3$	295	259	111	3	300	193				
AsCl$_3$	306	317	136	47	345	287	17	17	25	33
AsF$_3$			113	44			20	20	31	37
AsH$_3$	41	15			64	−41				
As(OC(CF$_3$)$_3$)$_3$	336	266	166	16	366	222	12	1	20	14
SbBr$_3$	323	312	181	79			27	26	40	51
Sb(C$_2$F$_5$)$_3$	319	274	164	45	340	215				
SbCl$_3$			174	76			26	25	39	51
SbF$_3$			157	74	348	279	34	32	46	54
SbH$_3$	90	99			122	53				
Sb(OC(CF$_3$)$_3$)$_3$			221	69	391	241	28	20	41	42
equatorial Lewis base binding in group 15 and 16										
S(C$_2$F$_5$)$_4$	349	307	87	−28	341	232				
SF$_4$	296	330	90	25	321	282	13	14	19	25
SH$_4$	53	65			67	67				
S(OC(CF$_3$)$_3$)$_4$	519	454	122	−31					−47	−44
Se(C$_2$F$_5$)$_4$	357	311	132	−28	368	252			13	13
SeF$_4$	334	356	150	25	373	321	26	26	41	52
SeH$_4$	101	111			118	53				
Se(OC(CF$_3$)$_3$)$_4$	497	426	*193*	38	505	357	−10	−13	*15*	18
Te(C$_2$F$_5$)$_4$	412	360	220	90	438	313	41	39	52	55
TeF$_4$	347	352	198	109	392	323	34	34	59	73
TeH$_4$	131	133	66	6	158	85				
Te(OC(CF$_3$)$_3$)$_4$	*473*	397	*253*	96	*503*	354	*23*	24	*59*	65
PBr$_3$	410	400	129	35	448	367	−100	−86	−23	6
P(C$_2$F$_5$)$_3$	341	304	49	−70	344	235			−132	−117
PCl$_3$	375	375	100	15	411	341			−36	−6
PF$_3$	218	252	1	−60	259	217			−86	−58
PH$_3$	26	51			55	8				
P(OC(CF$_3$)$_3$)$_3$	388	325	111	−33	412	273	−129	−122	−59	−46
AsBr$_3$	411	396	151	54	457	371	−74	−64	−7	20
As(C$_2$F$_5$)$_3$	332	292	63	−58	363	250				
AsCl$_3$	388	383	136	47	434	357	−72	−62	−9	18
AsF$_3$	277	305	71	4	321	270			−30	−10
AsH$_3$	41	15			70	−25				
As(OC(CF$_3$)$_3$)$_3$	422	350	162	7	457	306	−68	−74	−6	−4
SbBr$_3$	396	372	185	81	444	349	−30	−24	15	33
Sb(C$_2$F$_5$)$_3$	355	309	135	10	393	274			−38	−31
SbCl$_3$	377	361	174	76	425	337			14	32
SbF$_3$	300	304	132	51					14	27
SbH$_3$	90	99			122	53				
Sb(OC(CF$_3$)$_3$)$_3$	425	350	229	76	475	325	−12	−18	34	35
"special" Lewis acids										
Al(C$_5$F$_4$N)$_3$	526	444	414	253	578	419	138	144	179	193
Al(OC$_5$F$_4$N)$_3$	521	430	402	234	576	413	110	124	151	172
Al(OC(C$_6$F$_5$)$_3$)$_3$	*459*	351	*329*	141	*485*	305	*50*[a]	47	*76*[a]	79

Table 4. continued										
Compound axial Lewis base binding in group 15 and 16	HIA	HIA$_{solv}$	CIA	CIA$_{solv}$	MIA	MIA$_{solv}$	WA	WA$_{solv}$	AA	AA$_{solv}$
Al(OTeF$_5$)$_3$	534	469	408	263	593	454	131[a]	137	177[a]	189
F$_4$C$_6$(1,2-B(C$_6$F$_5$)$_2$)$_2$	535	459	331	174	505	359	22[a]	25	75[a]	89
F$_4$C$_6$(1,2-B(C$_{12}$F$_8$))$_2$	517	428	333	164	515	359	4[a]	11	75[a]	89
B(OC$_5$F$_4$N)$_3$	460	379	255	92	509	361	26[a]	51	91[a]	130
B(OTeF$_5$)$_3$	497	418	281	124	547	393	44[a]	47	111[a]	126
B(C$_6$F$_4$-pCF$_3$)$_3$	536	473	300	157	557	420	69[a]	70	139[a]	151
pentaphenylborole-F$_{25}$	534	450	311	152	567	408	65[a]	71	147[a]	162
As(OTeF$_5$)$_5$	676	589	383	221	719	556	75[a]	79	144[a]	156
Sb(OTeF$_5$)$_5$	705	630	460	301	771	624	117[a]	123	186[a]	202

Table 5. Correlation coefficients for the applied affinity scales.					
	FIA	HIA	CIA	MIA	WA
HIA	0.92				
CIA	0.93	0.81			
MIA	0.93	0.99	0.85		
WA	0.60	0.35	0.74	0.41	
AA	0.72	0.56	0.85	0.41	0.93

ments based on ion radii and Born's equation should be taken with caution, since explicit solvation effects might come into account. Interestingly, affinity solvation damping does not happen for the neutral Lewis bases, and water and ammonia affinities become even larger in solution. This effect can be ascribed to the poor solvation of H$_2$O and NH$_3$ in CH$_2$Cl$_2$ and the increased polarization/dipole moment of Lewis adducts, increasing the solvation free energy of the adducts in comparison to the sum of the less-polarized Lewis acid and base.[31] Plots of XIA$_{solv}$ against its respective vacuum XIA show in all cases a linear correlation. However, the correlation is more "broadened" for ionic XIAs than for neutral XIA scales, emphasizing the need to compute XIA$_{solv}$ to describe Lewis acidity adequately (Figure 4).
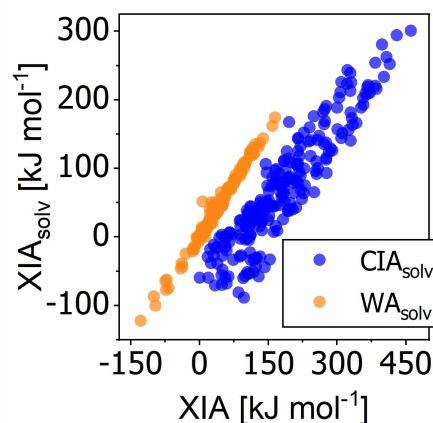
Figure 4. Correlation plots of the vacuum XIA against its respective XIA$_{solv}$, shown for water and chloride.

3. Conclusions

In the present paper, we extended the large-scale comparison of Lewis acids by methide, chloride, hydride, water, and ammonia affinities within accuracy to coupled-cluster values. Correlations and comparison plots tie connections between affinity scales and underscore the necessity of a multidimen-
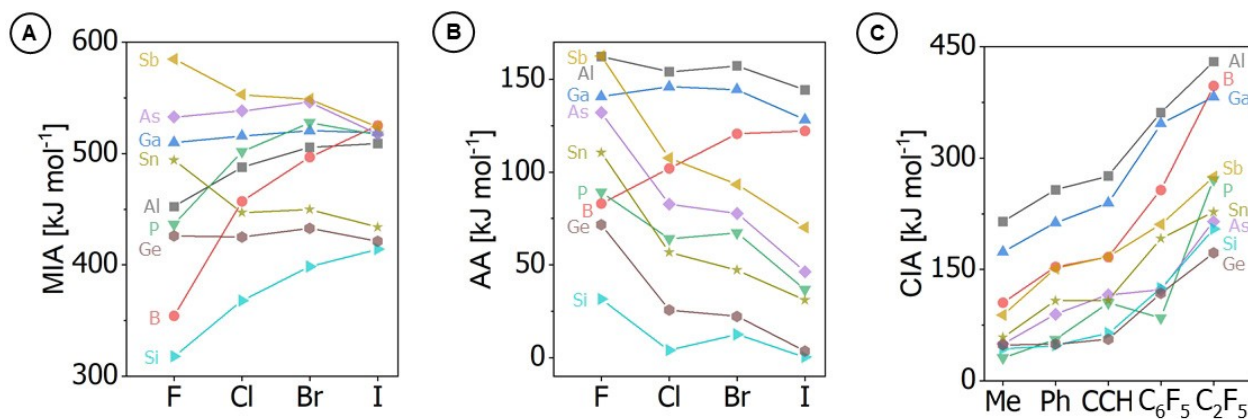
Figure 3. Representative comparison plots of different ligand classes: **A** propagation of MIA for halides, **B** propagation of AA for halides and **C** CIA for C-substituents.

sional picture of Lewis acidity. With the FIA, six metrics are now available to discuss Lewis acidity from a proper thermodynamic perspective and support future Lewis acid design.

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Conflict of Interest

The authors declare no conflict of interest.

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