SUPPORTING INFORMATION

Bond Dissociation Energies of Low-Valent Lanthanide Hydroxides: Lower Limits from Ion-Molecule Reactions and Comparisons with Fluorides

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Contents

Table S1. Results for reaction (3) with an OH-donor alcohol, and (3′) with OH-donor water.[a]

Ln^+	**R=H[b]** *BDE*=498.8	**R=C_6H_5[c]** *BDE*=474±8	**R=CH_3[c]** *BDE*=390±10	**R=CH_3CH_2[c]** *BDE*=392±4	**R=$(CH_3)_2CH$[c]** *BDE*=402±2
La^+	**Yes**	No/Other	**Yes**	**Yes**	**Yes**
Ce^+	No/Other	No/Other	**Yes**	**Yes**	**Yes**
Pr^+	**Yes**	No/Other	**Yes**	**Yes**	**Yes**
Nd^+	No/Other	**Yes**	**Yes**	**Yes**	**Yes**
Pm^+	NS	NS	NS	NS	NS
Sm^+	No/Other	**Yes**	**Yes**	**Yes**	**Yes**
Eu^+	**Yes[d]**	**Yes**	**Yes**	**Yes**	**Yes**
Gd^+	No/Other	No/Other	**Yes**	**Yes**	**Yes**
Tb^+	No/Other	No/Other	**Yes**	**Yes**	**Yes[f]**
Dy^+	**No**	No/Other	No/Other	**Yes**	**Yes**
Ho^+	**No**	No/Other	No/Other	**Yes**	No/Other
Er^+	**No**	No/Other	No/Other	**Yes**	No/Other
Tm^+	**Yes[d]**	**No/Other**	**No**	**No**	**No**
Yb^+	**Yes[e]**	**No**	**No**	**No**	**No**
Lu^+	No/Other	No/Other	**Yes**	**Yes**	**Yes**

[a] Results are for OH-abstraction: Yes = Observed; No = Not observed; No/Other = Possibly obscured by another reaction; NS = Not Studied. Red = also studied in the present work. Abstraction under thermal conditions indicates *BDE*[Ln^+-OH] ≥ *BDE*[R-OH] (given in kJ/mol[1]).

[b] SIFT results from Bohme, et al.[2]

[c] ICR results from Marçalo, et al.[3, 4] The reactant alcohols are phenol methanol, ethanol and isopropanol.

[d] QIT results from this work; reaction not seen by SIFT.[2]

[e] Confirmed in the present work by QIT.

Table S2. Reported reactions of lanthanide cations with halide donors.[a,b]

Ln^+	CH_3F	SF_6	C_6H_5F	CH_3Cl	C_6H_5Cl
La^+	✓	✓	✓	✓	✓
Ce^+	✓	✓	✓	✓	✓
Pr^+	✓	✓	✓	✓	✓
Nd^+	✓	✓	✓	✓	✓
Pm^+	-	-	-	-	-
Sm^+	✓	✓	✓	✓	✓
Eu^+	✓	✓	✓	✓	✓
Gd^+	✓	✓	✓	✓	✓
Tb^+	✓	✓	✓	✓	✓
Dy^+	✓	✓	✓	✓	✓
Ho^+	✓	✓	✓	✓	✓
Er^+	✓	✓	✓	✓	✓
Tm^+	✓[c]	✓	✓	✓[d]	✓
Yb^+	✓[c]	✓	✓	✓[d]	✓
Lu^+	✓	✓	✓	✓	✓
***BDE*[Ln^+-X][e]**	≥ 459±1	≥ 392±1	≥ 534±9	≥ 351±1	≥ 406±8

[a]A check mark (✓) indicates that abstraction of a halogen atom X from the donor RX to yield LnX^+ was observed; a dash (-) indicates that the reaction was not studied.
[b]Results are from: Ref.[5] for SF_6; Ref.[6] for CH_3F; Ref.[7] for CH_3Cl; Ref.[8] for C_6H_5Cl and C_6H_5F.
[c]Also studied by Cornehl et al. using FTICR-MS, with no reaction reported.[9]
[d]Product reported in Ref.[7] with only an upper limit given for the reaction rate.
[e]Lower limit for *BDE*[Ln^+-X] (kJ/mol) indicated for those Ln^+ that exhibit abstraction. *BDEs* for donors are from NIST Chemistry WebBook.[1]

Table S3. Assessed and computed *BDEs* (kJ/mol) for lanthanide diatomics.

	(1)	(1′)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Ln	***Ln^+-F^a C&C Pref.***	***Ln^+-F^a C&C Alt.***	***Ln^+-Cl^a C&C***	***Ln^+-F^b KHF***	***Ln^+-Cl^b KHF***	***Ln-F^a C&C***	***Ln-Cl^a C&C***	***Ln-OH^c Comp.***	***Ln-F^d Comp.***
La	695	*656*	529	659	504	644	500	560	672
Ce	678	*630*	512	612	429	626	490	553	665
Pr	669		493	611	445	604	470	481	589
Nd	639		471	602	441	580	448	445	567
Pm^e	623		459	601	435	566	436	452	569
Sm	609		455	607	435	556	431	437	528
Eu	594		442	584	431	550	419	426	554
Gd	671	*614*	491	589	404	615	467	531	596
Tb	648	*579*	476	621	417	604	457	679	794
Dy	584		436	535	408	547	412	577	567
Ho	596	*558*	435	513	410	558	418	586	698
Er	598	*555*	440	549	407	574	429	500	527
Tm	545		409	537	408	515	384	369	503
Yb	519		387	557	400	486	361	389	513
Lu	586	*481*	446	377	181	623	462	624	740

[a]From *C&C*:[10] *Preferred* (1) and *Alternate* (1′) for LnF^+ from Table 6; the two sets were obtained from *BDE*[Ln-F] using different values for IE[LnF]; (2) $LnCl^+$ from Table 6; (5) LnF from Table 4 recommended values; (6) LnCl from Table 3 third law values (other values there are similar).
[b]From *KHF* Table 5:[11] (3) and (4).
[c]From Dixon et al., 2017[12]: Table 7, reaction (3) R/UCCSD(T), and *BDE*[HO-OH] = 214.1 kJ/mol.[1]
[d]From Dixon et al., 2011:[13] Table 6, U/UCCSD(T), and *BDE*[CH_3-F] = 459.4 kJ/mol.[1]
[e]Values for Pm are purely estimates as there are no experimental data.

Table S4. Selected differences between *BDEs* in Table S3.

	(1)-(2) LnF^+-$LnCl^+$ ***C&C Pref.***	(1′)-(2) LnF^+-$LnCl^+$ ***C&C Alt.***	(3)-(4) LnF^+-$LnCl^+$ ***KHF***	(5)-(6) LnF-LnCl ***C&C***	(8)-(7) LnF-LnOH ***Computed***	(1)-(5) LnF^+-LnF ***C&C***
La	166	***127***	155	144	112	51
Ce	166	***118***	183	136	112	52
Pr	176		166	134	108	65
Nd	168		161	132	122	59
Pm	164		166	130	117	57
Sm	154		172	125	91	53
Eu	152		153	131	128	44
Gd	180	***123***	185	148	65	56
Tb	172	***103***	204	147	115	44
Dy	148		127	135	-10	37
Ho	161	***123***	103	140	112	38
Er	158	***115***	142	145	27	24
Tm	136		129	131	134	30
Yb	132		157	125	124	33
Lu	140	***35***	196	161	116	-37

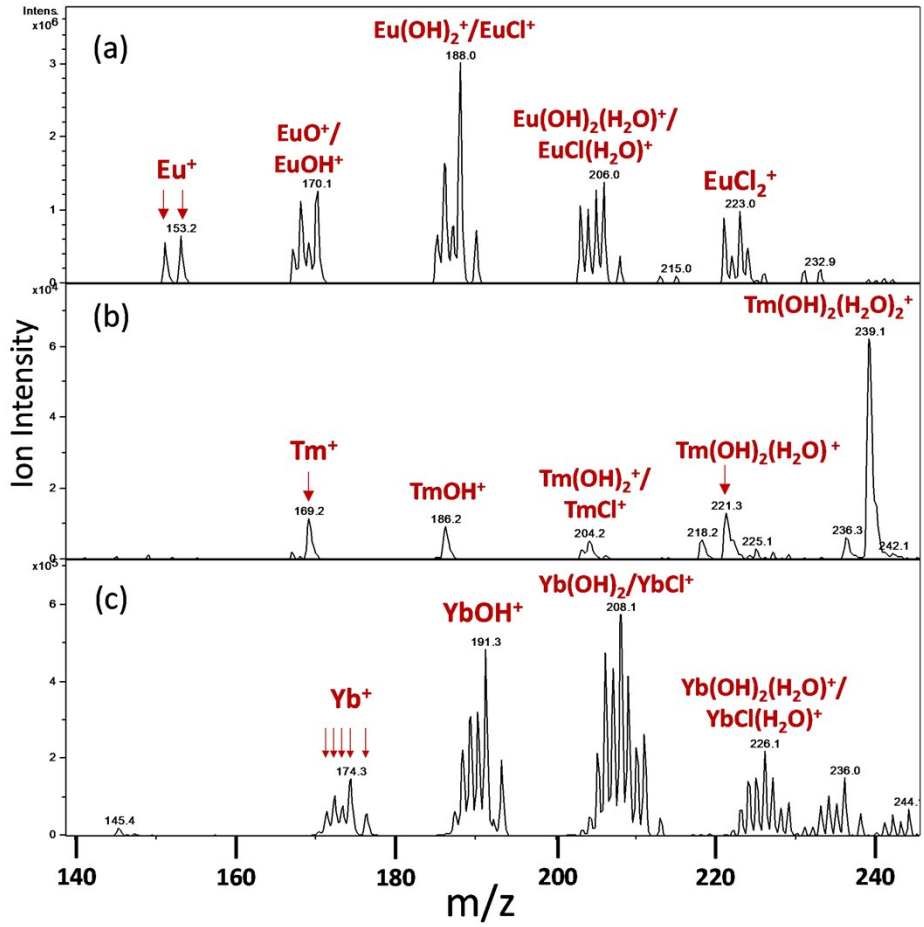

Figure S1. Representative ESI mass spectra for solutions of (a) $EuCl_3$; (b) $TmCl_3$; (c) $YbCl_3$, acquired before isolation of one isotope of bare Ln^+ for reactivity studies. Relative abundances of the various species can vary substantially upon changing experimental parameters such as the ESI and ion transfer voltages, and the ion trap drive. In contrast to products of ion-molecule reactions in the QIT, the species in these spectra were produced either during the ESI process or subsequently as a result of reactions during substantially hyperthermal ion transport from the ESI source to the ion trap.

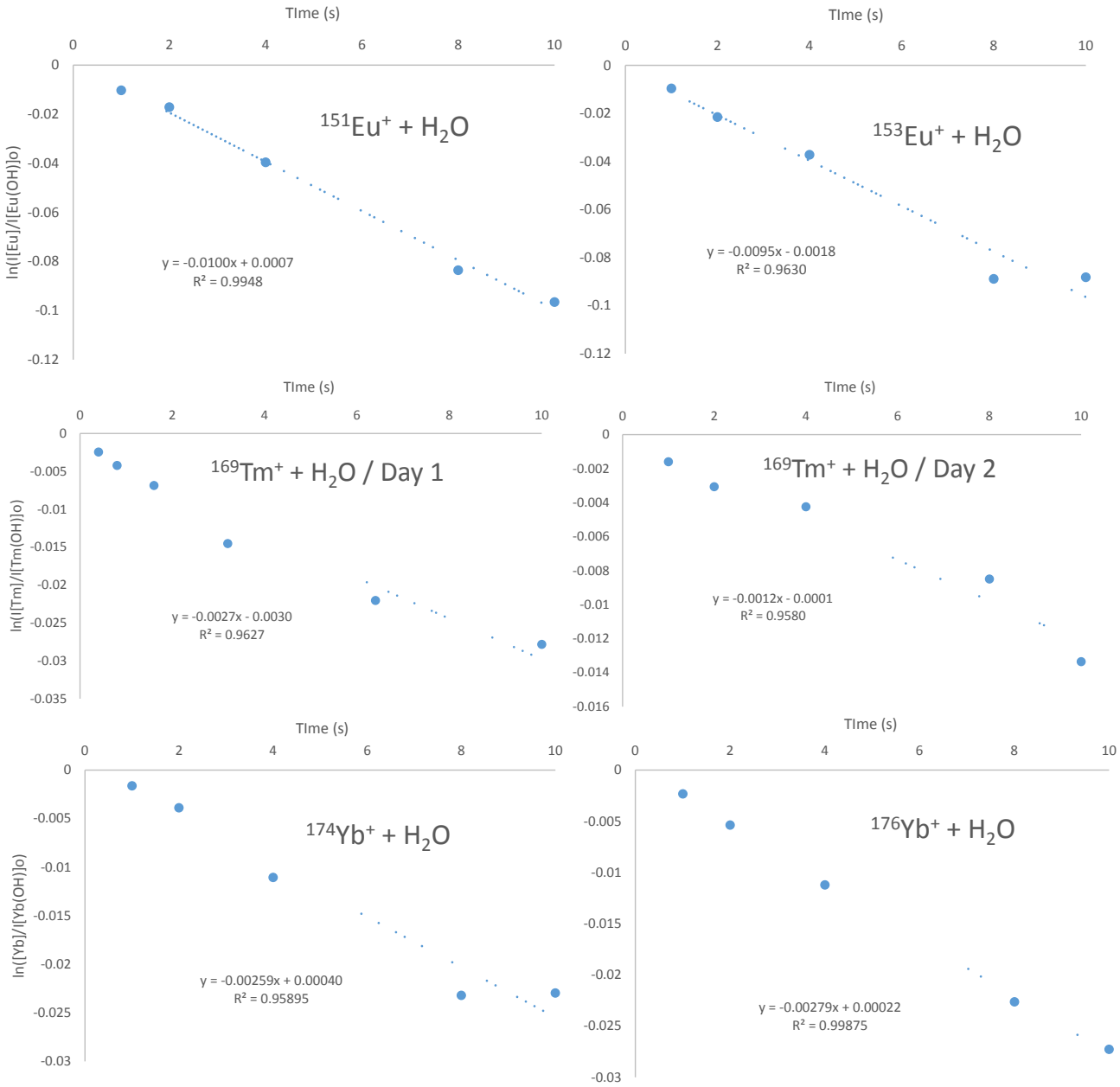

Figure S2. Kinetics results for reaction (3′) using the background water in the ion trap. Top: Two isotopes of Eu^+. Middle: $^{169}Tm^+$ on two days with different water pressures. Bottom: Two isotopes of Yb^+.

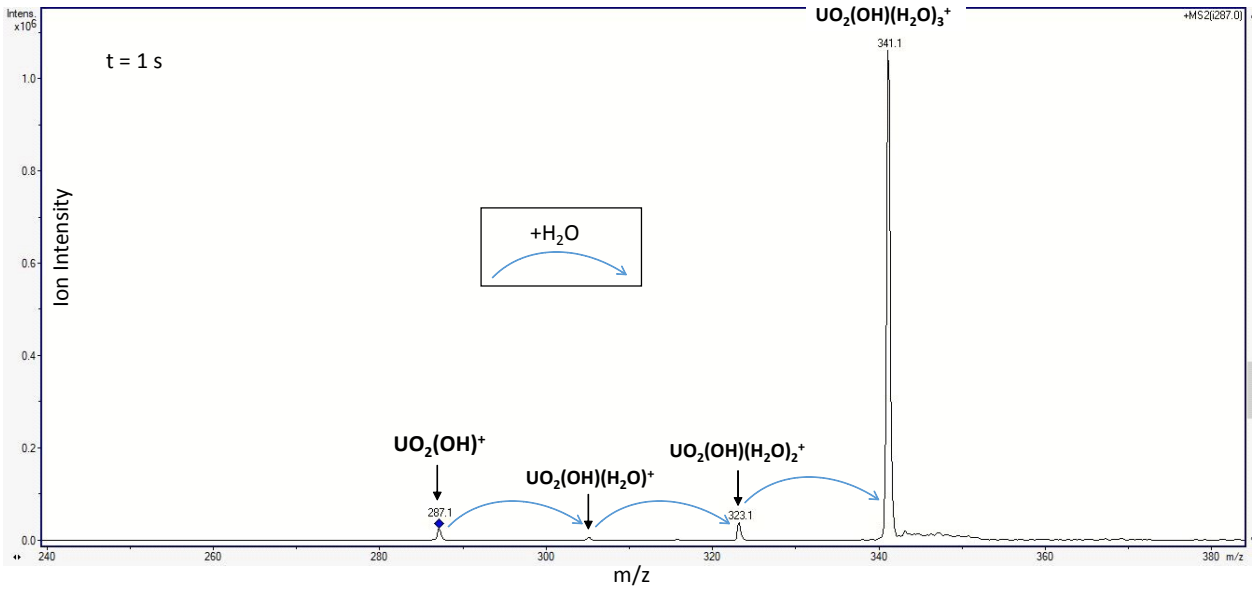

Figure S3. Mass spectrum acquired after isolation of $UO_2(OH)^+$ at 287 m/z for 1 s. Hydration to the terminal trihydrate at 341 m/z is >90% complete after the reaction with background water for 1 s. The primary hydration step employed to calibrate the variable water pressure in the trap is much faster than reaction (3′) for the bare Ln^+.

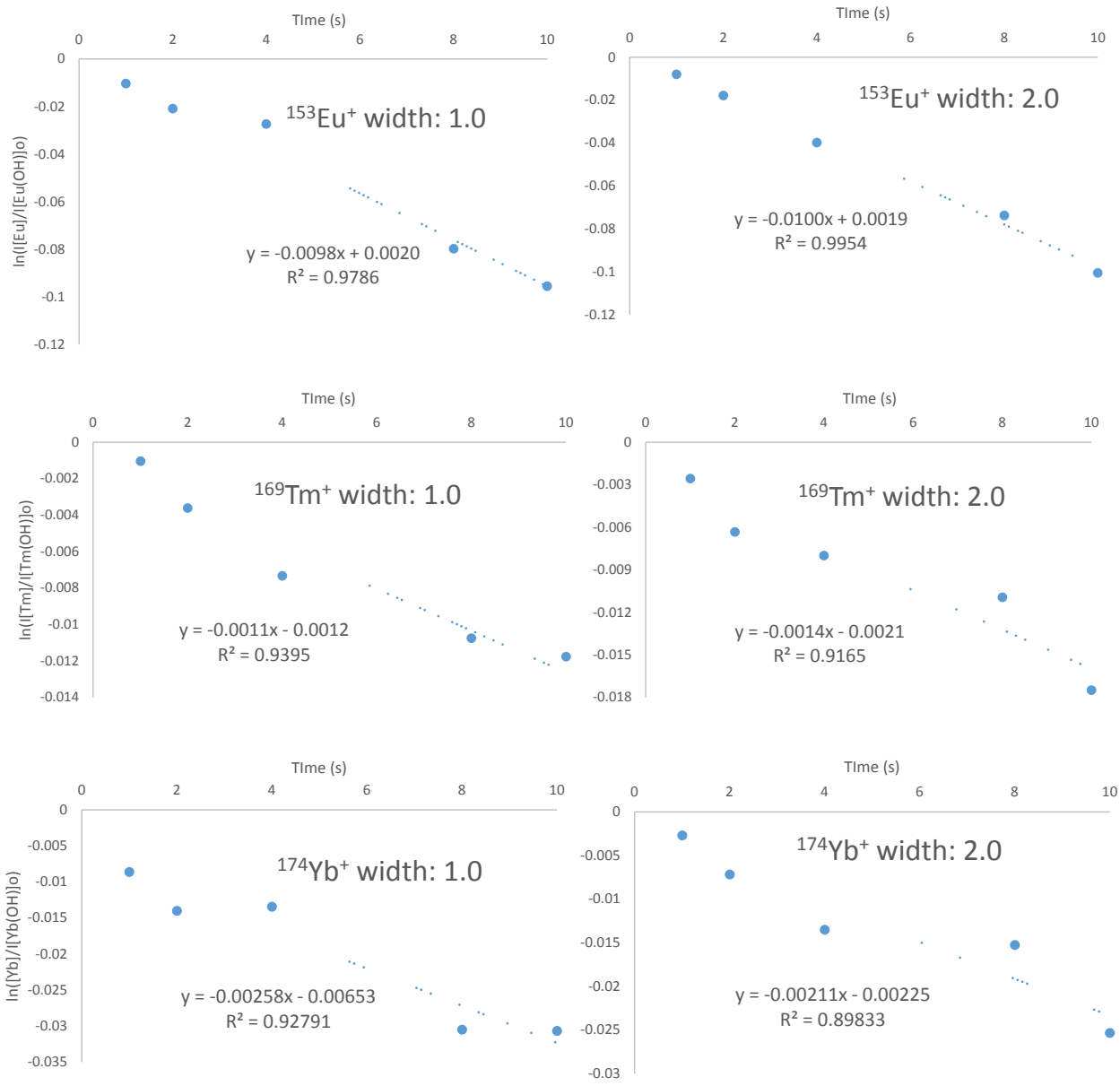

Figure S4. Reaction (3′) kinetics plots acquired for ion isolation widths (Δ*m/z*) of 1.0 and 2.0. The fitted slopes indicate essentially the same kinetics for the two isolation widths, and thus negligible effects of off-resonance ion excitation**.**

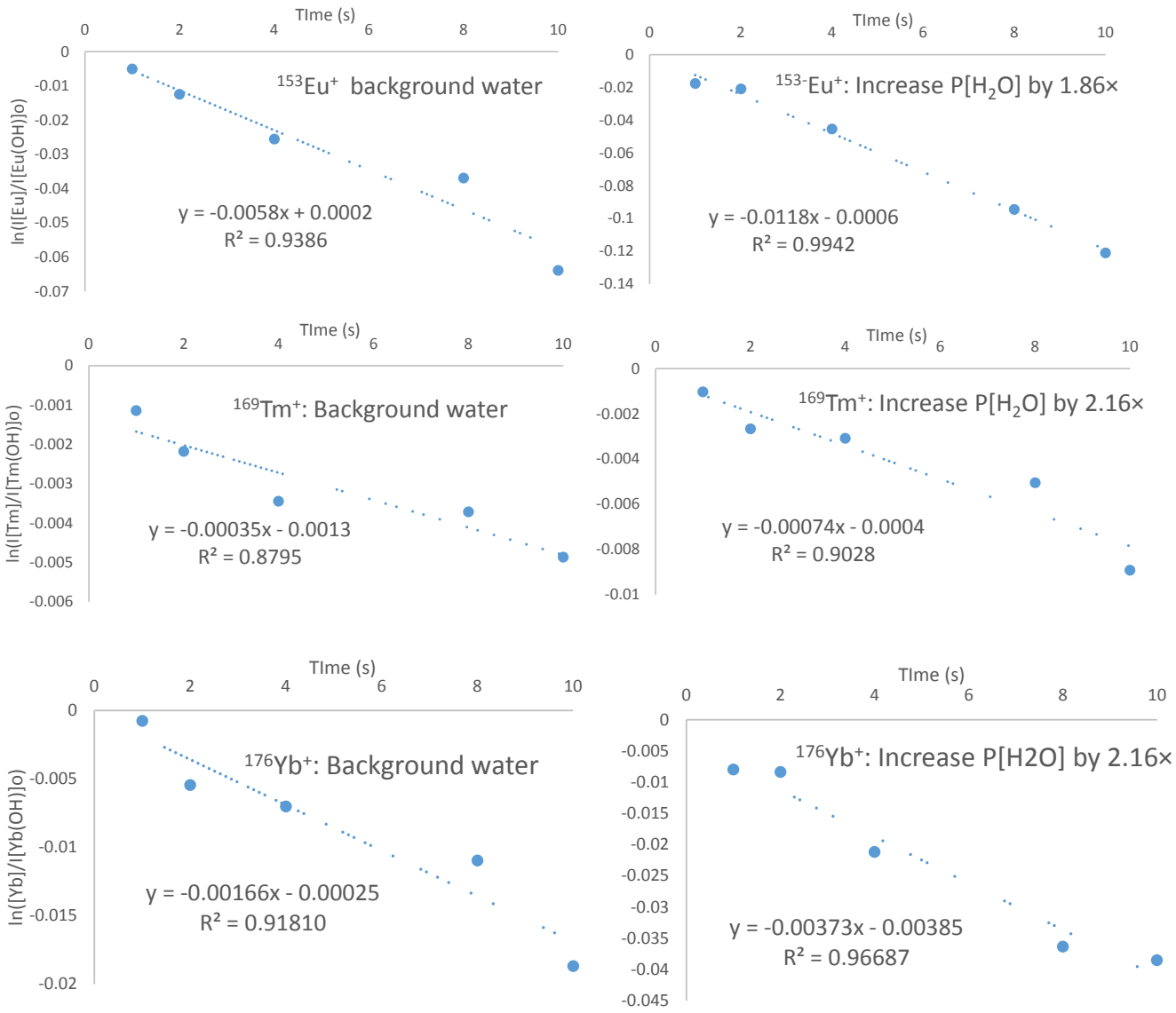

Figure S5. Reaction (3′) kinetics plots acquired using only background water in the ion trap (plots on left hand side), and after increasing the water pressure by the indicated factor (plots on right hand side; the P[H_2O] was increased by a factor of ~2×). The reaction rates increase as expected with increasing water pressure, confirming reaction (3′).

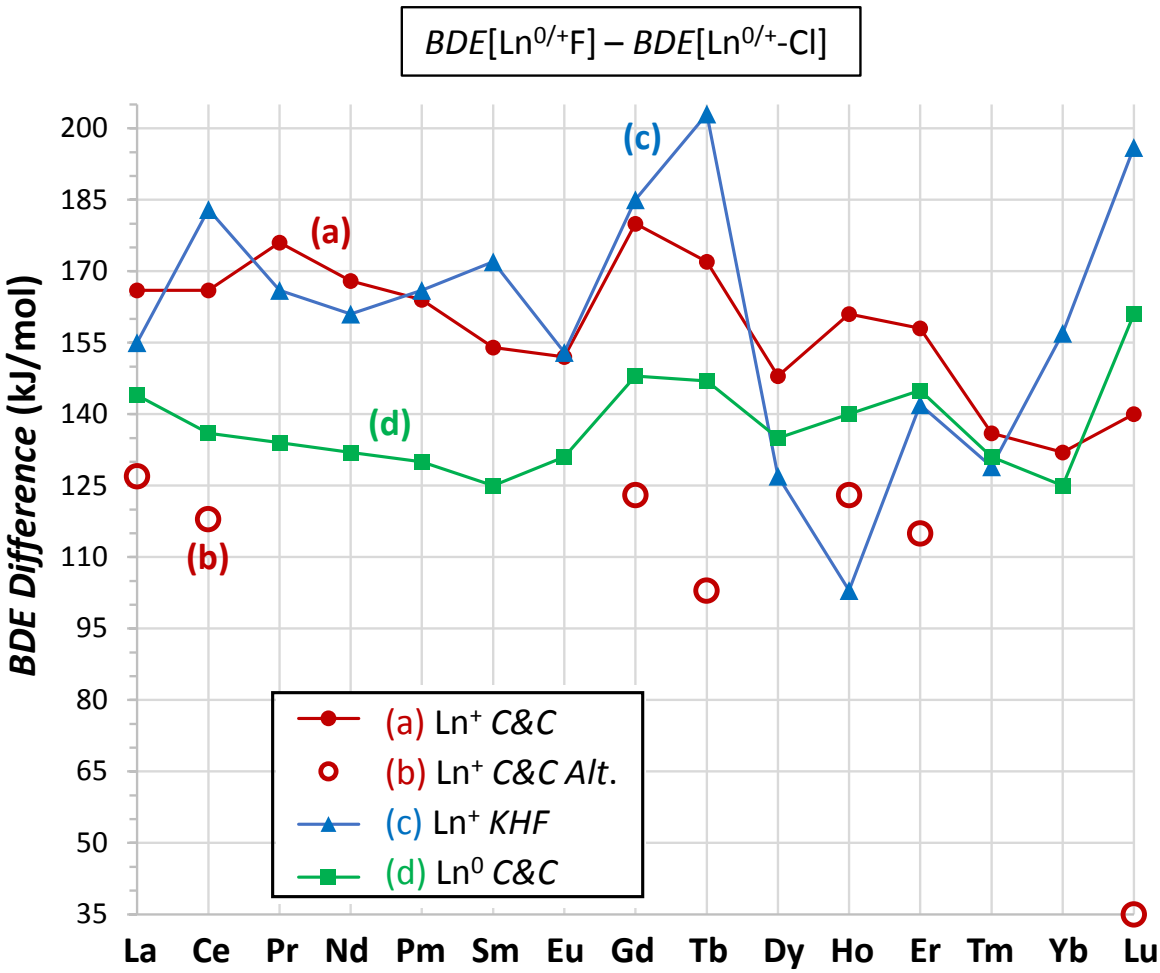

Figure S6. Difference between fluoride and chloride bond energies: *BDE*[$Ln^{0/+}$-F] - *BDE*[$Ln^{0/+}$-Cl] (differences in Table S3). (a) Solid red circles = cations LnX^+, using *preferred* fluoride values from *C&C* [(1)-(2)]; (b) Open red circles = cations LnX^+, using *alternate* fluoride values from *C&C* [(1′)-(2)]; (c) Solid blue triangles = cations LnX^+, using values from *KHF* [(3)-(4)]; (d) Solid green squares = neutrals LnX, using values from *C&C*.

As the bonding of lanthanides to fluorides and chlorides is presumed to be essentially of a comparable nature, the difference between fluoride and chloride *BDEs* is expected to be similar across the lanthanide series. For the neutral lanthanides ((d)/green squares) the difference *BDE*[Ln-F]-*BDE*[Ln-Cl] falls in the fairly narrow range of 125-148 kJ/mol, except for the larger difference of 161 kJ/mol for Lu. Variations in the cation lanthanide difference *BDE*[Ln^+-F]-*BDE*[Ln^+-Cl] are larger for than for neutrals. The cation difference is in the range of 132-180 kJ/mol using the *preferred* values from *C&C* ((a)/solid red circles). This range increases to 103-180 kJ/mol for the *alternate* values from *C&C*, excluding the very small difference of only 35 kJ/mol for Lu ((b)/open red circles). The cation difference using the *KHF* values ranges from 103-203 kJ/mol, with particularly large deviations for Tb, Ho and Lu. The smaller variation in *BDE*[Ln^+-F]-*BDE*[Ln^+-Cl] for the *preferred C&C* values (closed circles) versus *alternate C&C* values (open circles) is a primary criterion for assignment of values as “preferred”.

Estimation of hypothetical fully ionic BDE_{ionic}

An informative extreme model is that of fully ionic bonding. The goal here of considering such a model is not to accurately predict *BDEs* but rather to compare expected trends for such bonding with actual *BDEs*. In the ionic limit, neutral fluoride LnF is represented as $(Ln^{+})(F^{-})$ and cation LnF^{+} as $(Ln^{2+})(F^{-})$, as in reactions (S1) and (S2), respectively. The cation-anion interaction energy is given by the Coulomb equation: $E_C = -[1389.4\ (kJ/mol)(Å)/(e)^2][q_1q_2/r]$ where q_1 and q_2 are the charges on the two ions, and r is the distance between them. In addition to the energy gained by the Coulomb interaction, other components of fully ionic BDE_{ionic} are the ionization energy (IE) to create the cation and the electron affinity (EA), which is the energy gained in creating the anion; IE is defined as a positive quantity whereas EA is (usually) negative. To obtain E_C for LnF, $(Ln^{+})(F^{-})$, and LnF^{+}, $(Ln^{2+})(F^{-})$, we employ IE$[Ln^{+}]$ and IE$[Ln^{2+}]$ values from NIST,[14] and interatomic distances r derived as follows. A simple linear interpolation between computed distances for LaF (r = 2.02 Å) and LuF (r = 1.92 Å) was employed to obtain distances for the other LnF containing intermediate lanthanides between La and Lu.[15] The distances for LnF^{+} were then obtained from those for LnF by applying to all of the neutral distances the same 0.05 Å contraction that was computed for DyF^{+} versus DyF.[16] Without suggesting validity of the obtained absolute values for BDE_{ionic}, the results in Figure S7 demonstrate regular variations in E_C due to decreasing interatomic distance with increasing nuclear charge across the series. A key result is that the predicted variations in E_C are small relative to differences in ionization energies, such that the latter dominate variations in BDE_{ionic}.

(S1) $Ln + F \rightarrow (Ln^{+})(F^{-})$ $\quad\quad \Delta E = -BDE_{ionic}[Ln\text{-}F] = E_C + IE[Ln] + EA[F]$

(S2) $Ln^{+} + F \rightarrow (Ln^{2+})(F^{-})$ $\quad\quad \Delta E = -BDE_{ionic}[Ln^{+}\text{-}F] = E_C + IE[Ln^{+}] + EA[F]$

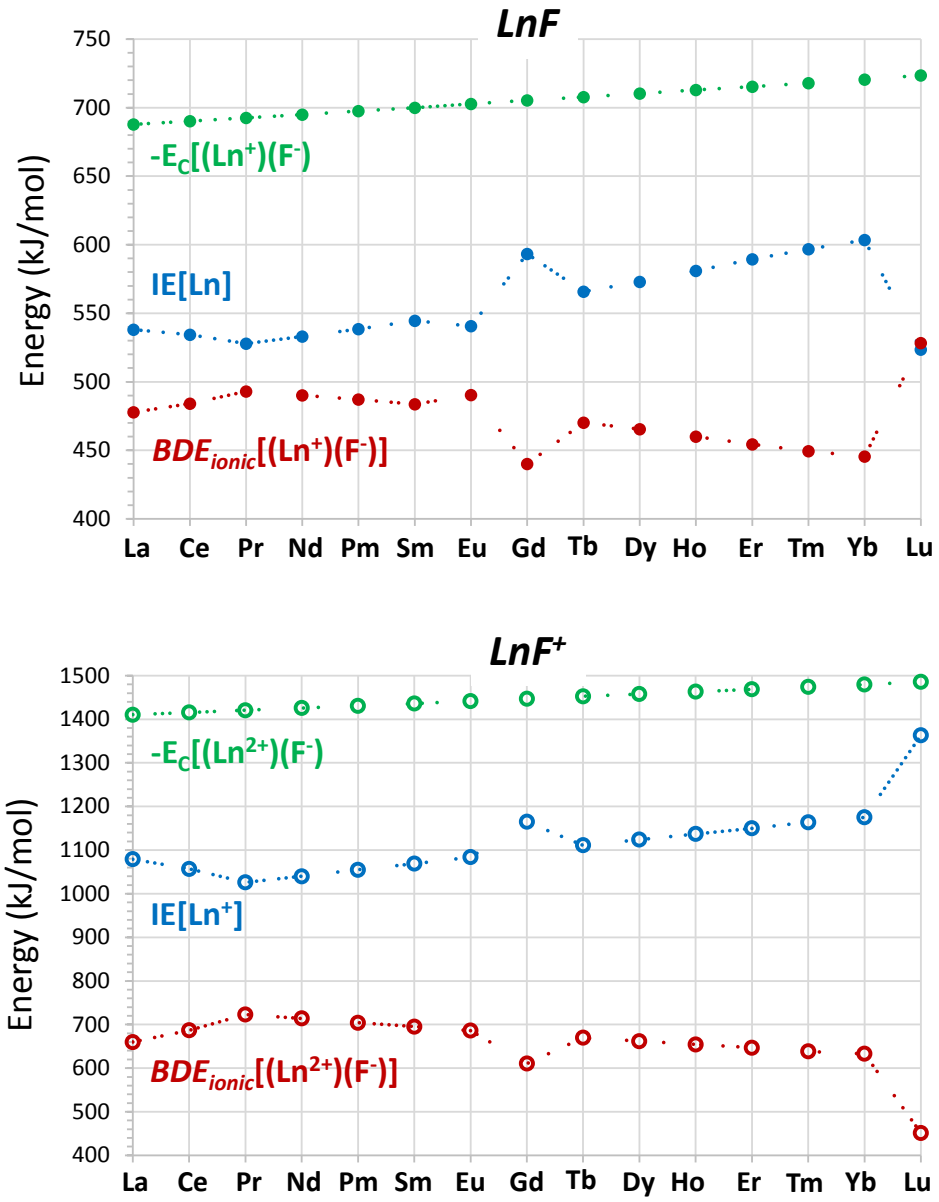

Figure S7. Dissociation energies BDE_{ionic} for LnF (in the top plots, red points) and LnF^+ (in the bottom plots, red points) obtained from the simple model of fully ionic bonding. Constituent ionization energies (IE, blue points) and Coulomb energies (E_C, green points) are also shown. The variations in E_C are much smaller and more regular than for the IEs, such that the variations in BDE_{ionic} primarily reflect those in IEs. Both IE[Lu] and IE[Lu^+], and the resulting BDE_{ionic} for LuF and LuF^+ are characteristically deviant. There are smaller but significant deviations for Gd.

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