Supporting information

A Cyclic Ion Mobility and DFT Study of the Structures, Isomer Space and Isomer Interconversion of Lanthanide Bromide Clusters, $Ln_xBr_{3x+1}^-$, x=1-6

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Table of Contents

1. $^{TW}CCS_{N2}$ values for $Ln_xCl_{3x+1}^-$ (ref. [1]) and comparison to $Ln_xBr_{3x+1}^-$ from present study

Table S1: Experimental travelling wave $^{TW}CCS_{N2}$ values for $Ln_xCl_{3x+1}^-$ anions (in Å^2). For $Ln_6Cl_{19}^-$ (Ln= Sm-Lu) we observe two peaks corresponding to two non-interconverting isomers. The relative intensities of the two isomers are given in brackets.

	$LnCl_4^-$	$Ln_2Cl_7^-$	$Ln_3Cl_{10}^-$	$Ln_4Cl_{13}^-$	$Ln_5Cl_{16}^-$	$Ln_6Cl_{19}^-$	
La	116.8	150.3	176.5	196.6	216.0	228.7 (100%)	
Ce	116.4	149.1	174.8	194.9	214.3	226.2 (100%)	
Pr	116.0	148.3	173.8	193.6	215.3	224.4 (100%)	
Nd	115.7	147.8	173.2	192.5	217.4	223.0 (100%)	
Sm	115.1	146.3	171.5	190.7	216.8	220.5 (94%)	225.5 (6%)
Eu	114.8	145.8	170.9	190.2	215.7	219.5 (89%)	224.3 (11%)
Gd	114.6	145.5	171.0	189.7	215.1	218.8 (80%)	223.6 (20%)
Tb	114.2	144.7	169.8	189.6	214.0	217.6 (69%)	222.4 (31%)
Dy	114.0	144.1	169.2	189.6	213.0	216.7 (55%)	221.4 (45%)
Ho	113.9	143.8	169.0	189.4	212.3	215.9 (47%)	220.6 (53%)
Er	113.7	143.6	168.8	189.5	211.7	215.5 (42%)	220.1 (58%)
Tm	113.5	142.8	167.7	189.0	210.7	214.4 (38%)	219.0 (62%)
Yb	113.3	142.4	167.4	188.8	210.2	214.1 (33%)	218.7 (67%)
Lu	113.1	142.7	167.5	188.8	209.5	213.4 (30%)	217.8 (70%)

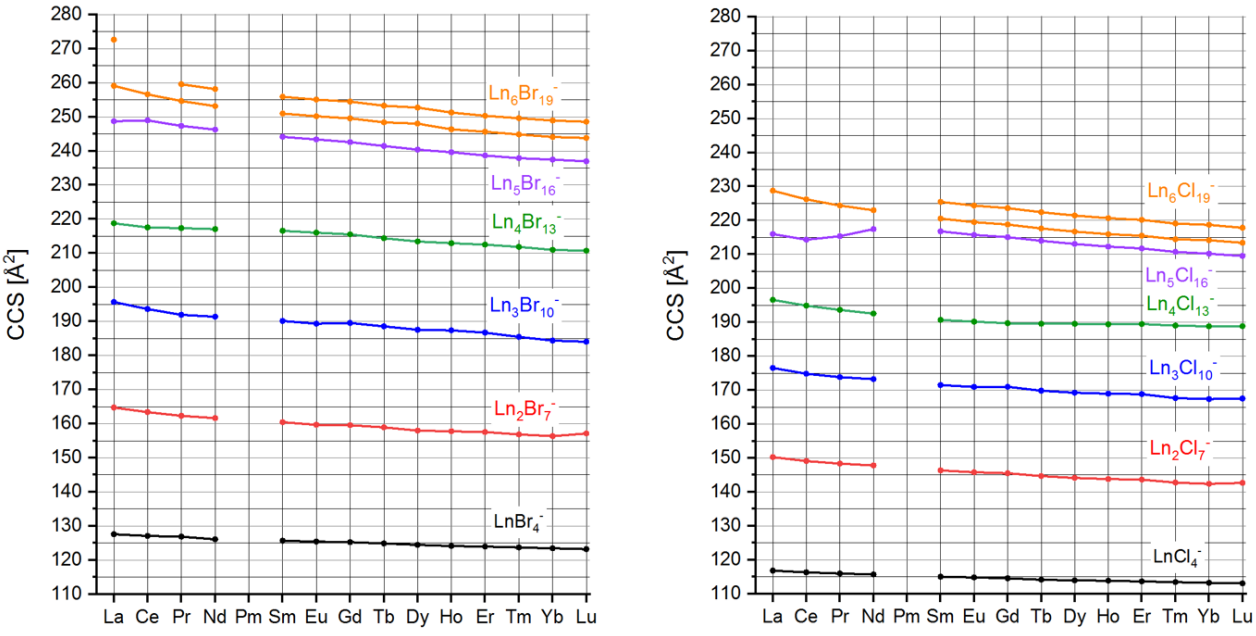
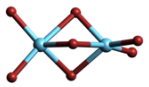


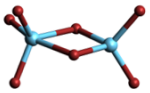
Figure S1: a) Collision cross sections $^{TW}CCS_{N2}$ of $Ln_xBr_{3x+1}^-$, x=1-6, Ln= La-Lu except Pm (see **Table 1**). b) Collision cross sections $^{TW}CCS_{N2}$ of $Ln_xCl_{3x+1}^-$, x=1-6, Ln= La-Lu except Pm for comparison

2. DFT calculated isomer energies and structures of $Ln_xBr_{3x+1}^-$

Table S2: Isomers of $Ln_2Br_7^-$, Ln= La-Lu. Energies at PBE/ECP/TZVP in kJ/mol (relative to isomer **A**). Energies for $Ln_2Cl_7^-$ in brackets for comparison

	B		C	
La	5.5	(5.5)	25.8	(32.2)
Ce	4.7	(4.7)	24.9	(31.4)
Pr	3.9	(3.9)	24.0	(30.6)
Nd	3.2	(3.2)	23.1	(29.8)
Sm	2.6	(2.8)	22.7	(29.4)
Eu	2.1	(2.2)	22.2	(28.9)
Gd	1.6	(1.7)	21.7	(28.5)
Tb	1.2	(1.3)	21.3	(28.1)
Dy	0.7	(0.8)	20.9	(27.7)
Ho	0.4	(0.5)	20.5	(27.5)
Er	-0.1	(0.1)	20.1	(27.2)
Tm	-0.7	(-0.5)	19.6	(26.8)
Yb	-1.0	(-0.8)	19.3	(26.6)
Lu	-1.8	(-1.5)	18.9	(26.0)

A 

B 

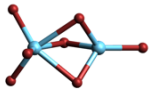
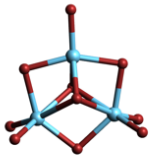
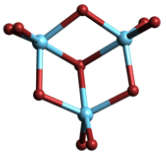
C 

Table S3: Isomers of $Ln_3Br_{10}^-$, Ln= La-Lu. Energies at PBE/ECP/TZVP in kJ/mol (relative to isomer **A**). Energies for $Ln_3Cl_{10}^-$ in brackets for comparison

	B		C	
La	22.9	(17.8)	22.0	(24.8)
Ce	22.4	(17.6)	22.8	(25.1)
Pr	22.3	(17.5)	23.8	(25.8)
Nd	22.4	(17.4)	24.5	(26.3)
Sm	22.2	(17.2)	24.8	(26.2)
Eu	22.0	(17.0)	24.8	(26.3)
Gd	21.8	(16.8)	24.2	(26.6)
Tb	21.7	(16.7)	23.5	(25.8)
Dy	21.5	(16.7)	22.8	(25.1)
Ho	21.2	(16.8)	22.1	(24.5)
Er	21.2	(16.6)	21.5	(23.9)
Tm	20.7	(16.2)	20.8	(23.0)
Yb	20.7	(16.2)	19.9	(22.3)
Lu	20.1	(15.6)	19.2	(21.4

A 

B 

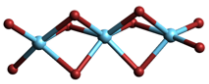
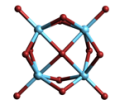
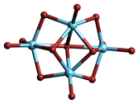
C 

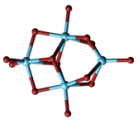
Table S4: Isomers of $Ln_4Br_{13}^-$, Ln= La-Lu. Energies at PBE/ECP/TZVP in kJ/mol (relative to isomer **A**).

Energies for $Ln_4Cl_{13}^-$ in brackets for comparison. Numbers in italics refer to structures with one imaginary frequency.

	B		C		D
La	3.2	(15.5)	45.6	(60.4)	*56.6*
Ce	0.0	(12.7)	44.3	(58.9)	*53.6*
Pr	-3.0	(10.1)	42.8	(57.2)	50.6
Nd	-5.5	(8.0)	42.0	(56.3)	48.0
Sm	-7.9	(6.1)	41.4	(55.9)	45.6
Eu	-10.5	(3.8)	41.1	(55.4)	43.2
Gd	-12.8	(1.9)	40.6	(54.9)	40.6
Tb	-15.1	(-0.1)	40.3	(54.5)	38.3
Dy	-17.4	(-2.1)	39.9	(54.0)	35.8
Ho	-19.2	(-3.7)	*39.7*	(53.6)	33.5
Er	-21.2	(-5.5)	*39.3*	(53.2)	31.0
Tm	-23.6	(-7.6)	*39.1*	(52.9)	28.4
Yb	-25.2	(-9.1)	*39.1*	(52.7)	26.1
Lu	-27.6	(-11.3)	*38.8*	(52.4)	23.3

A 

B 

C 

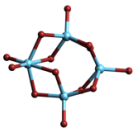
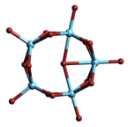
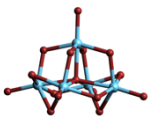
D 

Table S5: Isomers of $Ln_5Br_{16}^-$, Ln= La-Lu. Energies at PBE/ECP/TZVP in kJ/mol (relative to isomer **A**).

Energies for $Ln_5Cl_{16}^-$ in brackets for comparison

	B		C	
La	15.6	(-1.3)	14.6	(-1.2)
Ce	19.9	(2.4)	20.5	(4.0)
Pr	24.2	(6.1)	26.6	(9.3)
Nd	28.7	(10.0)	32.8	(14.7)
Sm	32.7	(13.9)	38.5	(20.2)
Eu	36.8	(17.8)	44.2	(25.7)
Gd	41.0	(21.8)	50.1	(31.4)
Tb	45.0	(25.6)	55.6	(36.7)
Dy	49.1	(29.9)	61.4	(42.5)
Ho	53.0	(33.8)	67.1	(48.1)
Er	56.8	(38.1)	72.5	(53.8)
Tm	60.5	(42.2)	77.8	(59.6)
Yb	64.3	(46.2)	83.4	(65.1)
Lu	67.7	(50.3)	88.1	(70.7)

A 

B 

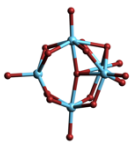
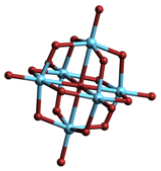
C 

Table S6: Isomers of $Ln_6Br_{19}^-$, Ln= La-Lu. Energies at PBE/ECP/TZVP in kJ/mol (relative to isomer **A**).

Energies for $Ln_6Cl_{19}^-$ in brackets for comparison

	B		C	
La	6.4	(21.3)	17.5	(33.7)
Ce	5.5	(20.3)	19.3	(35.7)
Pr	4.9	(19.5)	21.9	(38.7)
Nd	4.2	(18.5)	23.5	(40.2)
Sm	3.4	(17.5)	24.4	(41.0)
Eu	2.4	(16.5)	25.0	(41.8)
Gd	1.7	(15.6)	26.4	(43.2)
Tb	0.7	(14.5)	26.9	(43.7)
Dy	-0.1	(13.5)	27.8	(44.6)
Ho	-0.5	(12.9)	29.5	(45.9)
Er	-1.3	(12.0)	30.3	(46.9)
Tm	-2.1	(11.0)	31.0	(47.5)
Yb	-2.6	(10.3)	32.2	(48.6)
Lu	-3.5	(9.3)	32.8	(49.3)

A



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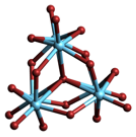

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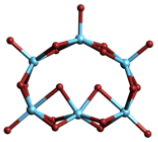


3. Calculated barrier heights for $Ln_2Br_7^-$, $Ln_3Br_{10}^-$, $Ln_4Br_{13}^-$ and $Ln_6Br_{19}^-$

Table S7. Energies (in kJ/mol) of the transition state from A to B relative to isomer A at level PBE for x=2-4, 6, i.e. $Ln_2Br_7^-$, $Ln_3Br_{10}^-$, $Ln_4Br_{13}^-$ and $Ln_6Br_{19}^-$. The respective chloride energies in brackets for comparison

	n=2		n=3		n=4		n=6	
La	10.1	(10.9)	29.0	(25.2)	77.4	(90.5)	75.4	(82.9)
Ce	9.4	(10.2)	29.0	(25.2)	74.0	(87.3)	76.5	(86.3)
Pr	8.8	(9.4)	28.9	(25.1)	70.6	(84.2)	82.7	(90.0)
Nd	8.2	(8.9)	28.8	(25.1)	67.7	(81.6)	86.3	(93.3)
Sm	7.8	(8.6)	28.8	(25.2)	65.1	(79.4)	89.5	(96.6)
Eu	7.4	(8.1)	28.9	(25.2)	62.4	(76.8)	92.7	(99.8)
Gd	7.0	(7.7)	29.0	(25.2)	59.8	(74.4)	96.3	(103.2)
Tb	6.7	(7.4)	29.1	(25.4)	57.3	(72.0)	99.3	(106.1)
Dy	6.3	(7.1)	29.2	(25.5)	54.8	(69.6)	102.7	(109.4)
Ho	6.0	(6.8)	29.3	(25.8)	52.4	(67.5)	106.4	(112.9)
Er	5.7	(6.4)	29.2	(25.8)	50.0	(65.0)	109.6	(116.1)
Tm	5.2	(6.0)	29.1	(25.8)	47.4	(62.4)	112.7	(119.3)
Yb	5.0	(5.8)	29.1	(26.0)	45.1	(60.4)	112.9	(122.5)
Lu	4.5	(5.3)	28.8	(25.6)	42.7	(57.7)	118.7	(125.4)

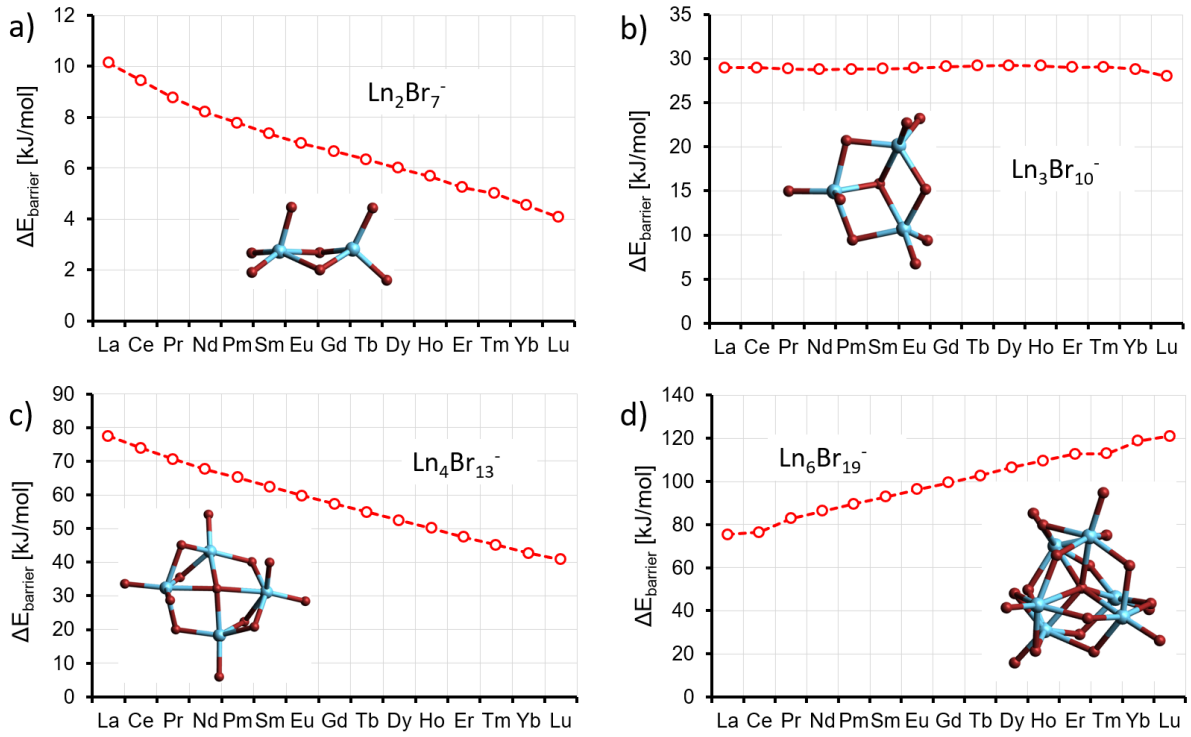


Figure S2: Calculated barrier heights between the two lowest energy isomers (**A** and **B**) with isomer **A** as reference for a) $Ln_2Br_7^-$, b) $Ln_3Br_{10}^-$, c) $Ln_4Br_{13}^-$, d) $Ln_6Br_{19}^-$.

4. IMS^2: Ejection-reinjection experiment for $Ln_6Br_{3x+1}^-$ isomers (Ln = Nd-Tm)

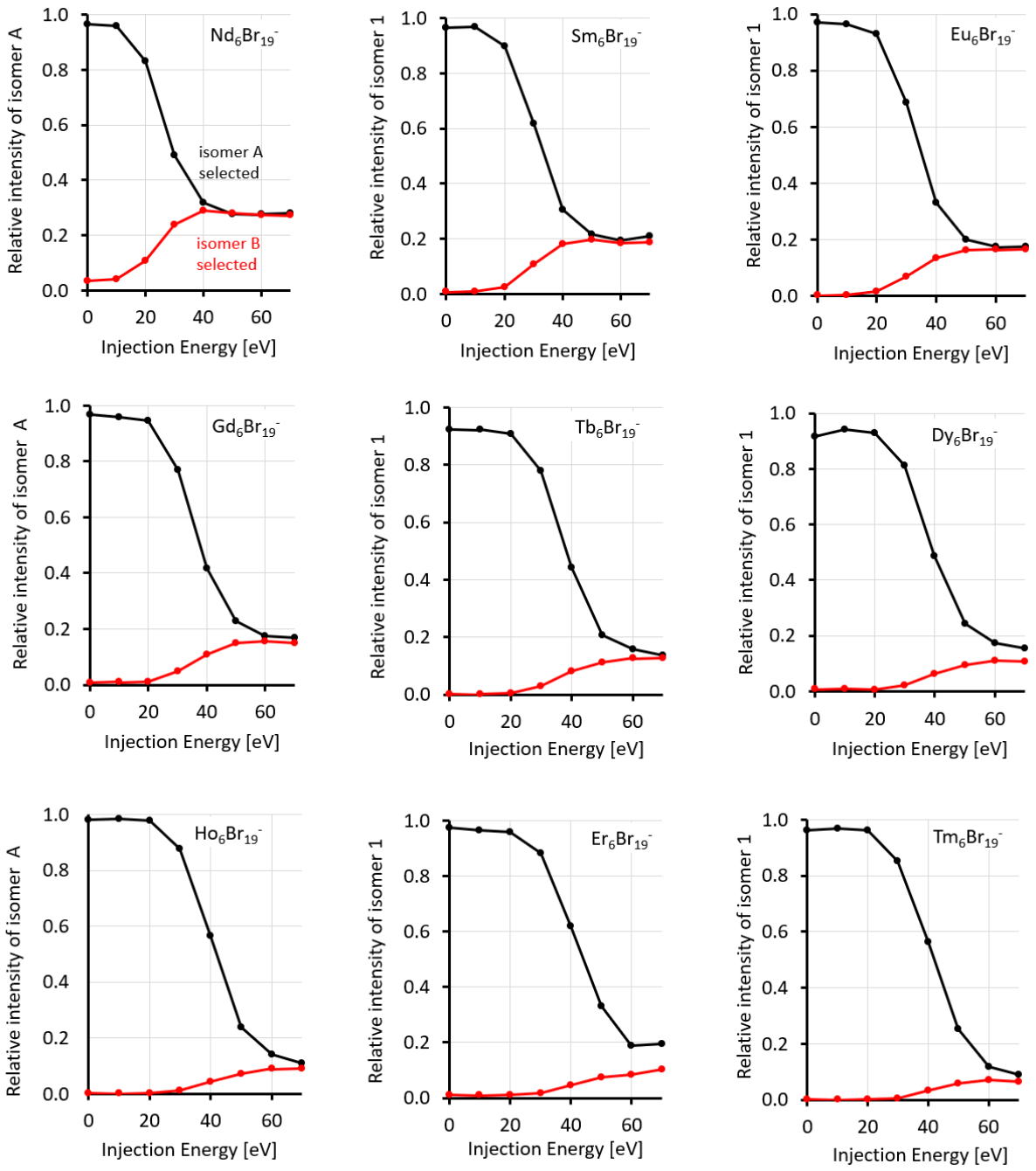


Figure S3: IMS-IMS experiments for $Ln_6Br_{19}^-$: (Ln= Nd-Tm): Isomer distribution as function of injection energy, black: isomer **A** selected, red: isomer **B** selected.

5. 1-5 cycles measurement for as prepared $Ce_6Br_{19}^-$ (showing slow forward isomerization)

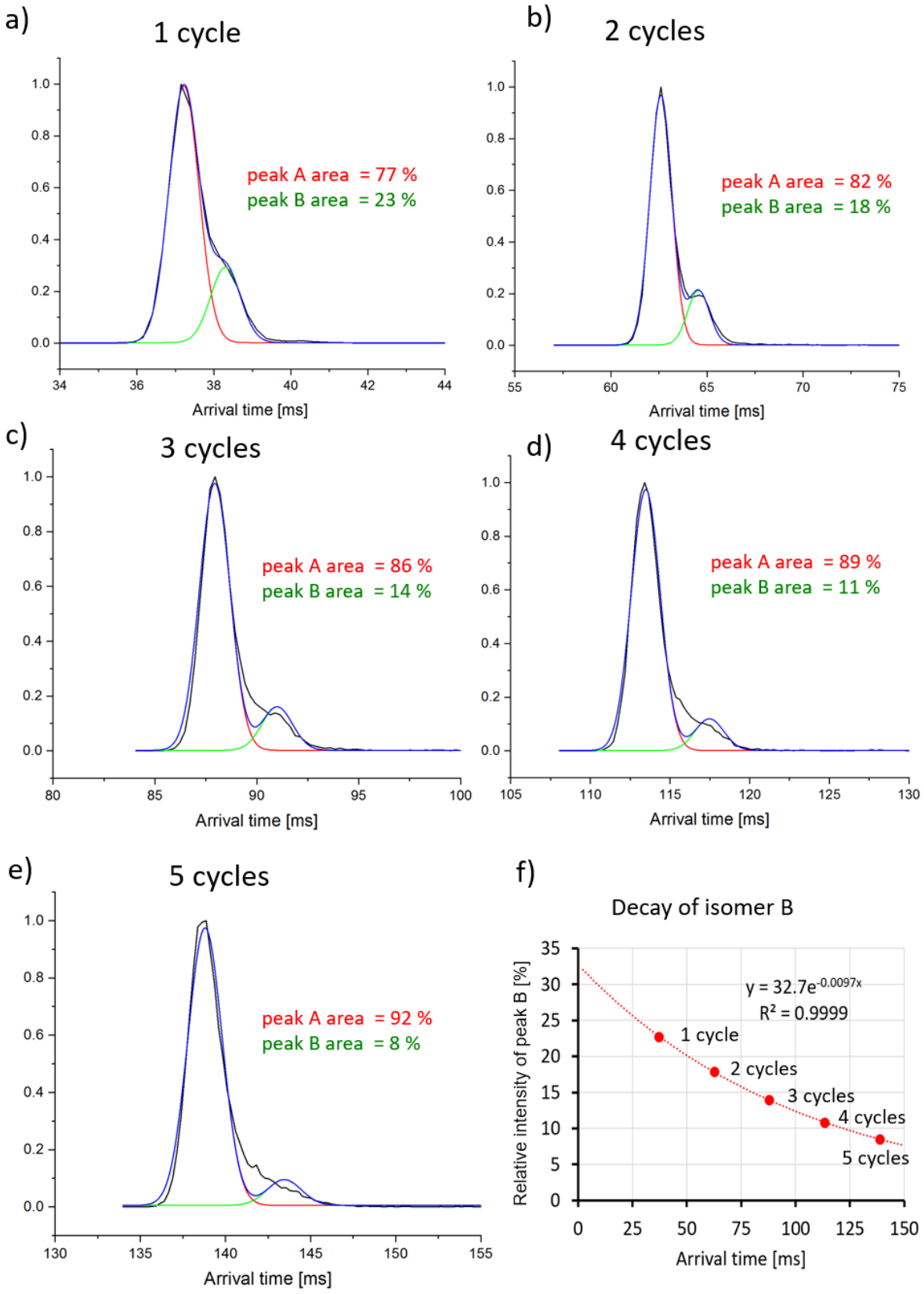


Figure S4: 1-5 cycles arrival distributions of $Ce_6Br_{19}^-$: fitting two Gaussians (with same width) to the data, a)-e) 1 - 5 cycles, f) kinetic fit based on the ratio of the peak areas. The decay rate constant obtained is 0.0097 ms^{-1} (9.7s^{-1}). The filling of the gap between the peaks is due to ion that undergo isomer interconversion during the drift time.

6. Isomer Interconversion of $Pr_6Br_{19}^-$

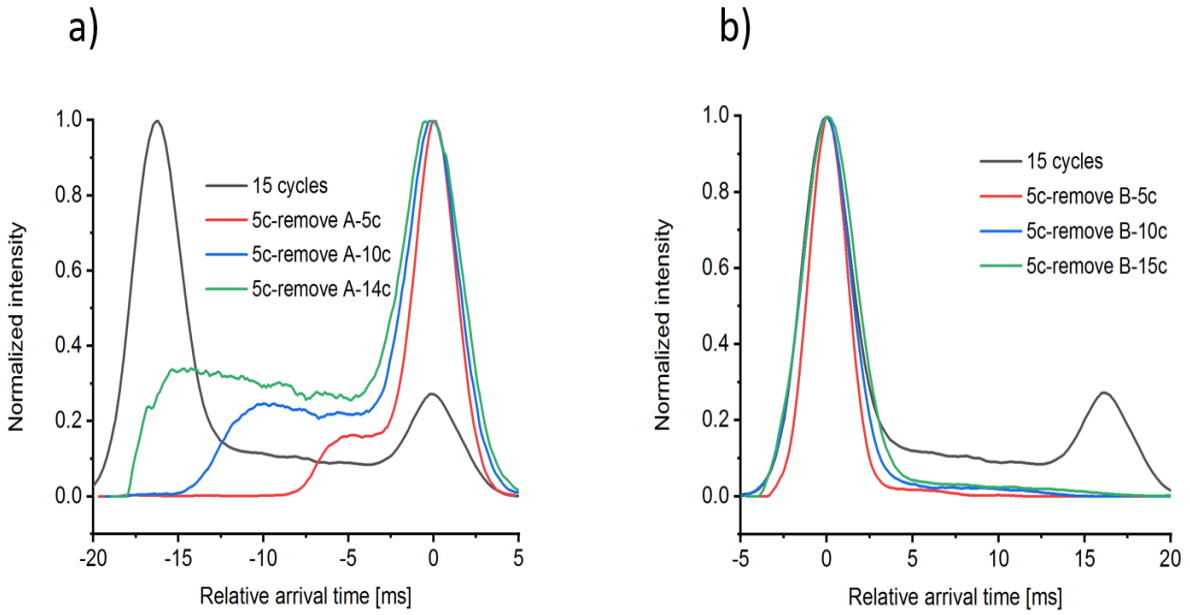


Figure S5: $Pr_6Br_{19}^-$: Raw data documenting workflow to determine isomer interconversion rate constants. a) Selection of isomer **B** and reappearance of isomer **A**: Black: standard 5-cycles IMS experiment, for comparison. Red: Isomer **A** removed after 5-cycles-separation followed by another 5-cycles-separation step. Blue and green, second step 10 and 14 cycles long, respectively. The shoulder grows towards the first peak (isomer **A**). All arrival time distributions are referenced (shifted) to the position of isomer **B** to facilitate comparison. b) Selection of isomer **A** and reappearance of isomer **B**. Black: standard IMS experiment, 5-cycles-separation, for comparison. Red: 5-cycles-separation then peak 2 is removed, then 5-cycles-separation. Blue and green, 10 and 15 cycles, respectively. The tailing slowly grows into the position of isomer **B**. All arrival time distributions are referenced (shifted) to the position of isomer **A** to facilitate comparison.

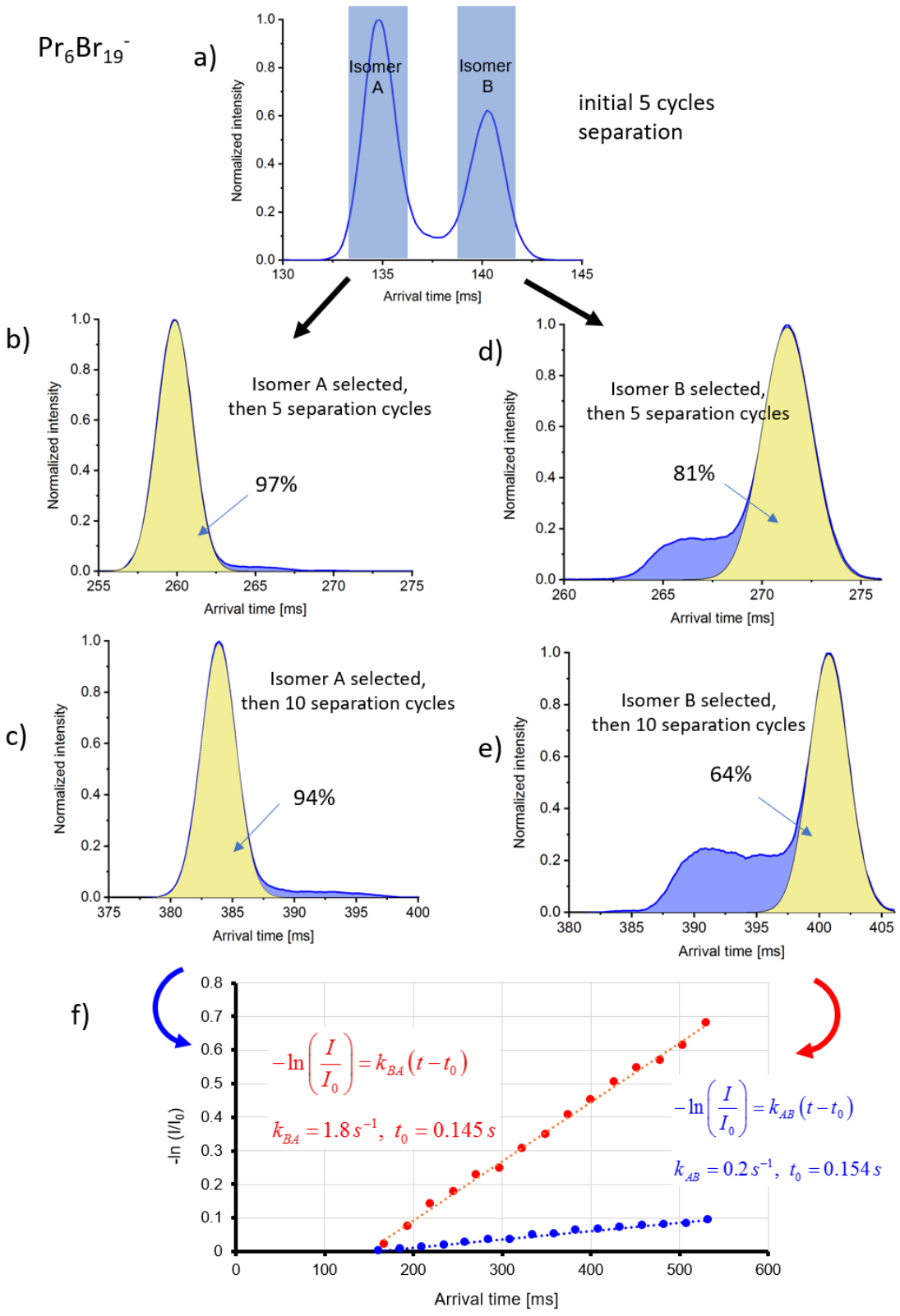
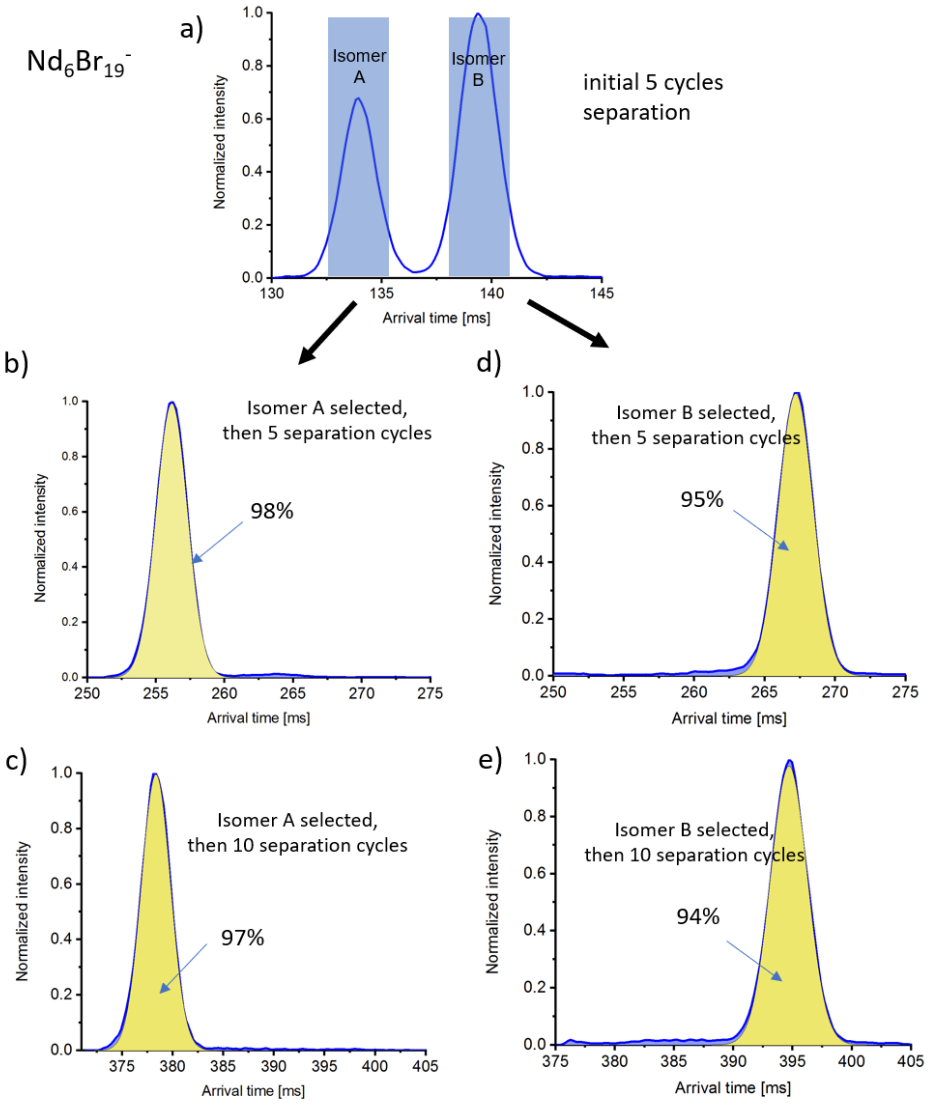


Figure S6: $Pr_6Br_{19}^-$: Isomer interconversion, quantitative analysis. a) Isomer distribution after 5-cycles-separation. After the separation step, either isomer **A** or isomer **B** is retained (marked areas), the rest of the ion distribution is removed. b) Arrival time distribution of isomer **A** after 5 cycles. The fraction of the isomer **A** ions that pass the drift cell without isomer conversion should correspond to a gaussian distribution therefore its relative area is obtained by fitting a Gaussian to the leading part of the arrival time distribution. The tail (blue) corresponds to ions that have undergone at least one conversion and therefore spend a fraction of their drift time as isomer **B**. c) same for 10 cycles. d) + c) same after selection of isomer **B**, 5 cycles and 10 cycles respectively. f) 1st order kinetics plot of the intensities obtained (I_0= total ion intensity, I - unreacted ions). See also **table S8**.

Table S8: $Pr_6Br_{19}^-$: Isomer interconversion, quantitative peak analysis (see also **figure S6** and **figure 14**). After 5 cycles of isomer selection, either isomer A or isomer B is selected. The relative intensity of the respective unreacted (=not converted) isomer as function of the arrival time is obtained by fitting a gaussian to the arrival time distributions.

Isomer A selected				Isomer B selected		
cycle #	arrival time (peak max) [ms]	relative intensity of unreacted isomer A [%]		cycle #	arrival time (peak max) [ms]	relative intensity of unreacted isomer B [%]
1	161	99.9		1	168	98.0
2	186	99.2		2	194	92.8
3	210	98.8		3	220	86.8
4	235	98.1		4	245	83.8
5	259	97.4		5	271	81.2
6	285	96.6		6	297	78.0
7	309	96.6		7	323	73.6
8	334	95.3		8	349	70.6
9	359	94.9		9	375	66.7
10	384	93.9		10	401	63.9
11	409	93.7		11	427	60.4
12	433	93.1		12	452	58.0
13	458	92.7		13	478	56.6
14	483	92.5		14	504	54.2
15	508	92.2		15	530	50.7

7. Isomer Interconversion of $Nd_6Br_{19}^-$?



Rate too small to determine,

$k_{AB}, k_{BA} < 0.1\ s^{-1}$

Figure S7: $Nd_6Br_{19}^-$: Isomer interconversion, quantitative peak analysis. a) Isomer distribution after 5-cycles-separation. After the separation step, either isomer **A** or isomer **B** is retained (marked areas), the rest of the ion distribution is removed. b) Arrival time distribution of isomer **A** after 5 cycles. The fraction of the isomer **A** ions that pass the drift cell without isomer conversion should correspond to a gaussian distribution therefore its relative area is obtained by fitting a Gaussian to the leading part of the arrival time distribution. The tail (blue) corresponds to ions that have undergone at least one conversion and therefore spend a fraction of their drift time as isomer **B**. c) same for 10 cycles. d) + c) same after selection of isomer **B**, 5 cycles and 10 cycles respectively. It turns out that the interconversion rates are to small to determine.

8. Isomer Interconversion – simulation of peak shape

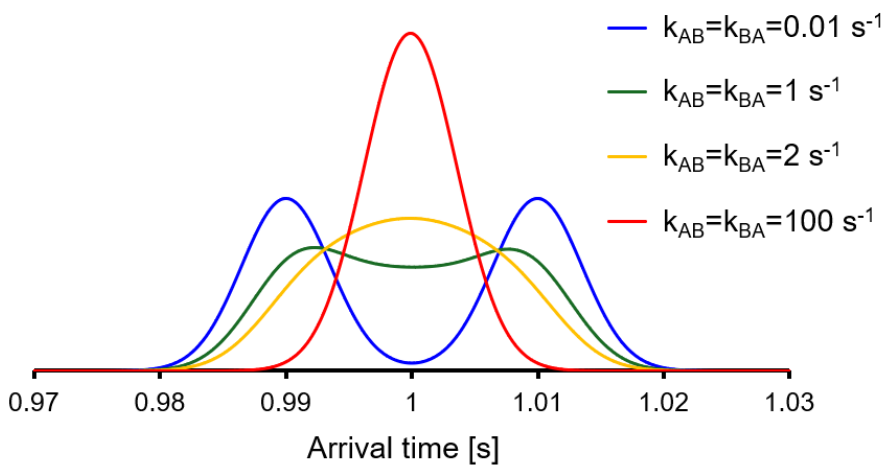


Figure S8: Simulated arrival time distributions (according to ref. [12] of the main text) for two interconverting isomers $A \rightleftharpoons B$ with equal interconversion rate constants k_{AB} and k_{BA}. Blue: interconversion much slower than the arrival time: two narrow peaks are resolvable. Red: interconversion much faster than the arrival time: one narrow peak at intermediate arrival time is observed. Green and yellow: interconversion time scale comparable to the arrival time: peak broadening

For two species, in the limit of slow interconversions two sharp peaks are observable. In the limit of fast interconversions one sharp peak at the weighted average of the individual arrival times is observable.

9. Reference for Supporting Information

1. Y. Nakajima, P. Weis, F. Weigend, M. Lukanowski, F. Misaizu and M. M. Kappes, Lanthanide chloride clusters, $Ln_xCl_{3x+1}^-$, x=1-6: an ion mobility and DFT study of isomeric structures and interconversion timescales*, Phys. Chem. Chem. Phys.*, 2025, **27**, 1017-1030.

10. DFT-optimized Coordinates for $La_xBr_{3x+1}^-$

(PBE/ECP/TZVP, in Å)

$LaBr_4^-$

La	-0.0000000	-0.0000000	0.0000000
Br	1.6387414	-1.6387414	1.6387414
Br	-1.6387414	1.6387414	1.6387414
Br	-1.6387414	-1.6387414	-1.6387414
Br	1.6387414	1.6387414	-1.6387414

$La_2Br_7^-$

isomer A

La	0.0023702	2.0529022	0.0082242
La	-0.0023931	-2.0529226	0.0082287
Br	1.9171419	0.2429638	-1.2161091
Br	0.0006586	-0.0001435	2.2264663
Br	-1.9177824	-0.2428002	-1.2150140
Br	1.7308761	-3.8095329	-1.3611312
Br	-1.5752696	-3.8849296	1.4490015
Br	1.5753118	3.8847919	1.4490959
Br	-1.7308967	3.8096860	-1.3609101

isomer B

La	0.0004508	2.1166092	0.0102961
La	0.0085317	-2.4820754	-0.0370213
Br	2.2783114	3.0250019	1.3802377
Br	0.0545280	-0.4732212	1.9981293
Br	0.0089406	-0.3399096	-1.9804193
Br	2.3097722	-4.0722340	-0.1432928
Br	-2.3186127	-4.0365975	-0.0779504
Br	-2.3995117	2.9031752	1.2354721
Br	0.0509576	3.6290943	-2.3657188

isomer C

La	-0.0000000	0.0000000	2.3707344
La	-0.0000000	0.0000000	-1.7413941
Br	-0.0000000	0.0000000	5.2042171
Br	1.1621733	2.0129431	0.7615195
Br	1.1621733	-2.0129431	0.7615195
Br	-2.3243465	0.0000000	0.7615195
Br	-1.2901029	-2.2345237	-2.8609302
Br	-1.2901029	2.2345237	-2.8609302
Br	2.5802057	0.0000000	-2.8609302

transition state A-B

La	2.0623681	0.1315481	0.1271314
La	-2.2813441	-0.2436427	-0.2169082
Br	0.9558062	2.1718416	1.7107932
Br	-0.2165739	0.6216128	-2.0463580
Br	-0.2494970	-1.8436911	1.0767430
Br	-3.8324109	1.5923415	1.2210466
Br	-4.0203479	-1.9482649	-1.5897077
Br	3.8122900	1.0988969	-1.8630364
Br	3.7697094	-1.5806421	1.5802963

La3Br10-

isomer A

La	0.0000000	-2.2824288	1.0759759
La	-0.0000000	-0.0000000	-2.5257291
La	0.0000000	2.2824288	1.0759759
Br	0.0000000	-2.9008027	-1.9279401

Br	-2.2228564	-3.7803655	1.8635339
Br	-0.0000000	-0.0000000	3.0324644
Br	2.2228564	-3.7803655	1.8635339
Br	-0.0000000	-0.0000000	-5.3306062
Br	-2.2228564	3.7803655	1.8635339
Br	2.2228564	3.7803655	1.8635339
Br	1.9698755	-0.0000000	-0.3251785
Br	0.0000000	2.9008027	-1.9279401
Br	-1.9698755	-0.0000000	-0.3251785

isomer B

La	1.3764150	2.3840207	-0.0325743
La	1.3764150	-2.3840207	-0.0325743
La	-2.7528300	0.0000000	-0.0325743
Br	2.2175404	-3.8408927	2.1942274
Br	0.0000000	0.0000000	-1.5719757
Br	3.0615404	0.0000000	0.6653187
Br	2.2175404	3.8408927	2.1942274
Br	2.1973470	3.8059166	-2.2789286
Br	-1.5307702	2.6513718	0.6653187
Br	-4.4350808	0.0000000	2.1942274
Br	-1.5307702	-2.6513718	0.6653187
Br	-4.3946940	0.0000000	-2.2789286
Br	2.1973470	-3.8059166	-2.2789286

isomer C

La	4.0770632	-0.0446699	-0.0082805
La	-0.0000217	0.1213591	0.0000324
La	-4.0770249	-0.0446883	0.0082416
Br	5.9986689	0.9389648	-1.8054650
Br	2.1146761	1.2493965	1.8481143
Br	-1.9797297	-2.1735440	0.1945324
Br	5.6714265	-1.2585043	1.9523897
Br	1.9796948	-2.1735078	-0.1943509
Br	-5.9986984	0.9390408	1.8053150
Br	-5.6713355	-1.2586077	-1.9524043
Br	-2.1147025	1.2493991	-1.8481489
Br	-1.9093994	1.2159152	1.9417712
Br	1.9093702	1.2158184	-1.9417422

transition state A-B

La	-2.4322761	1.1912766	0.2600032
La	0.0000002	-2.5927162	-0.3344522
La	2.4322755	1.1912770	0.2600031
Br	-2.8948881	-1.7482915	-0.1047182
Br	-4.1024339	2.0823792	-1.7878466
Br	-0.0000004	2.7395680	-0.5960098
Br	-3.5530186	2.1315667	2.6248364
Br	0.0000011	-5.3235763	0.2656571
Br	4.1024347	2.0823770	-1.7878469
Br	3.5530178	2.1315677	2.6248362
Br	-0.0000002	-0.2858115	1.6961115
Br	2.8948882	-1.7482911	-0.1047181
Br	-0.0000003	-1.8513255	-3.0158558

$La_4Br_{13}^-$

isomer A

La	-2.1495364	-2.1495364	-0.0409177
La	-2.1495364	2.1495364	-0.0409177
La	2.1495364	2.1495364	-0.0409177
La	2.1495364	-2.1495364	-0.0409177
Br	-3.5025353	0.0000000	-1.7298211

```
Br    0.0000000    3.5025353   -1.7298211
Br   -2.7921827    0.0000000    1.9679979
Br    0.0000000   -3.5025353   -1.7298211
Br    0.0000000   -2.7921827    1.9679979
Br    0.0000000    2.7921827    1.9679979
Br   -4.1195894   -4.1195894    0.0649470
Br    0.0000000    0.0000000   -0.9279775
Br    2.7921827    0.0000000    1.9679979
Br    4.1195894   -4.1195894    0.0649470
Br   -4.1195894    4.1195894    0.0649470
Br    3.5025353    0.0000000   -1.7298211
Br    4.1195894    4.1195894    0.0649470
isomer B
La    0.0000000   -2.2158401   -1.0312739
La    0.0000000    2.2158401   -1.0312739
La    3.2969832   -0.0000000    0.9713276
La   -3.2969832   -0.0000000    0.9713276
Br    0.0000000   -0.0000000    1.3110701
Br    0.0000000   -4.1186208   -3.0572193
Br    2.4270198   -2.8893382    0.5231428
Br   -2.4270198   -2.8893382    0.5231428
Br    1.8858447   -0.0000000   -2.0320362
Br    2.4270198    2.8893382    0.5231428
Br    3.7409409   -0.0000000    3.7172224
Br    5.8094660   -0.0000000   -0.2255797
Br   -1.8858447   -0.0000000   -2.0320362
Br    0.0000000    4.1186208   -3.0572193
Br   -2.4270198    2.8893382    0.5231428
Br   -3.7409409   -0.0000000    3.7172224
Br   -5.8094660   -0.0000000   -0.2255797
isomer C
La   -0.0076649    2.3612021   -0.1549298
La    0.0000000   -0.0000000   -3.7437820
La    0.0076649   -2.3612021   -0.1549298
La   -0.0000000    0.0000000    3.6334635
Br    0.0000000   -0.0000000   -6.5236886
Br   -1.8821535    1.9287714   -2.5144500
Br   -0.1313095    5.1266236   -0.4537804
Br    1.8821535   -1.9287714   -2.5144500
Br    1.8730463    1.9471025   -2.4918567
Br    0.1122996    2.8831439    2.7714083
Br    1.8197311   -0.0352506    0.8565208
Br   -1.8730463   -1.9471025   -2.4918567
Br   -0.1122996   -2.8831439    2.7714083
Br   -1.8197311    0.0352506    0.8565208
Br    2.2538246   -0.1181571    5.2853789
Br   -2.2538246    0.1181571    5.2853789
Br    0.1313095   -5.1266236   -0.4537804
transition state A-B
La   -2.4899200    1.5093662   -0.4946389
La    2.0774440    2.6103353    0.4408825
La    2.4889044   -1.5065409   -0.5158208
La   -2.0752394   -2.6125433    0.4389042
Br    0.9118314    3.4659699    2.8352395
Br    3.6780898    0.2407775    1.5381801
Br   -0.3709325    3.4688682   -1.1390417
Br   -3.6685974   -0.2479691    1.5568440
Br   -2.4846932   -0.7922293   -2.1939051
Br    2.4747224    0.8040100   -2.2030007
```

Br	-4.6660828	3.1254023	-1.1081040
Br	0.0028201	-0.0027385	0.8090713
Br	0.3668943	-3.4644685	-1.1547481
Br	-4.0108642	-4.4945894	-0.2459198
Br	4.0080204	4.4991128	-0.2396011
Br	-0.9038357	-3.4830778	2.8249050
Br	4.6614383	-3.1196851	-1.1492465

$La_5Br_{16}^-$

isomer A

La	-0.0000000	0.0000000	3.7686106
La	0.0000000	-3.2629764	1.1270377
La	-0.0000000	-2.2077482	-3.0937262
La	-0.0000000	2.2077482	-3.0937262
La	0.0000000	3.2629764	1.1270377
Br	-0.0000000	0.0000000	0.3833096
Br	-0.0000000	0.0000000	6.5472211
Br	-1.9746212	2.1474687	3.0703225
Br	1.9677162	-3.2892643	-1.1639366
Br	1.9746212	-2.1474687	3.0703225
Br	0.0000000	-5.9511824	1.8170958
Br	-1.9746212	-2.1474687	3.0703225
Br	-1.9677162	-3.2892643	-1.1639366
Br	-1.9430967	0.0000000	-3.6101266
Br	1.9430967	0.0000000	-3.6101266
Br	0.0000000	-3.8211611	-5.3417954
Br	0.0000000	3.8211611	-5.3417954
Br	-1.9677162	3.2892643	-1.1639366
Br	0.0000000	5.9511824	1.8170958
Br	1.9746212	2.1474687	3.0703225
Br	1.9677162	3.2892643	-1.1639366

isomer B

La	-2.5165337	2.1105727	0.7409997
La	-2.5165337	-2.1105727	0.7409997
La	2.5165337	-2.1105727	0.7409997
La	0.0000000	-0.0000000	-2.9049149
La	2.5165337	2.1105727	0.7409997
Br	-4.4206327	-0.0000000	-0.2108146
Br	-4.2666098	-4.1500373	1.4199342
Br	-4.2666098	4.1500373	1.4199342
Br	-2.4315089	-0.0000000	2.9143787
Br	0.0000000	-3.5630413	1.5567094
Br	4.2666098	-4.1500373	1.4199342
Br	2.4315089	-0.0000000	2.9143787
Br	0.0000000	-0.0000000	0.2163548
Br	1.9675326	-2.2078635	-2.2081935
Br	-1.9675326	-2.2078635	-2.2081935
Br	0.0000000	-0.0000000	-5.6865731
Br	1.9675326	2.2078635	-2.2081935
Br	4.4206327	-0.0000000	-0.2108146
Br	0.0000000	3.5630413	1.5567094
Br	4.2666098	4.1500373	1.4199342
Br	-1.9675326	2.2078635	-2.2081935

isomer C

La	2.3533924	-0.3322669	2.1634978
La	2.3533924	-0.3322669	-2.1634978
La	0.0916873	3.0023206	-0.0000000
La	-3.6246778	0.6164651	-0.0000000
La	-1.2038620	-3.0675541	-0.0000000

Br	0.7440076	-2.8808742	2.3323228
Br	-1.9101098	-5.7533504	-0.0000000
Br	4.0889474	-0.6089381	4.3113747
Br	1.0650405	2.2243486	-2.8789207
Br	-2.3765593	2.5728814	-1.8267443
Br	3.1328495	1.7741369	-0.0000000
Br	1.0650405	2.2243486	2.8789207
Br	-0.0770969	-0.1141161	-0.0000000
Br	4.0889474	-0.6089381	-4.3113747
Br	3.8283468	-1.7848347	-0.0000000
Br	-2.3765593	2.5728814	1.8267443
Br	0.7440076	-2.8808742	-2.3323228
Br	-3.0722521	-1.6577368	1.8988272
Br	-6.3680685	1.0352422	-0.0000000
Br	-3.0722521	-1.6577368	-1.8988272
Br	0.5479790	5.7405194	-0.0000000

$La_6Br_{19}^-$

isomer A

La	3.5258610	-0.0000000	-0.0000000
La	0.0000000	0.0000000	-3.5258610
La	-0.0000000	-3.5258610	0.0000000
La	0.0000000	0.0000000	3.5258610
La	0.0000000	3.5258610	0.0000000
La	-3.5258610	0.0000000	-0.0000000
Br	0.0000000	-6.2851364	0.0000000
Br	-0.0000000	-2.9278226	-2.9278226
Br	6.2851364	-0.0000000	0.0000000
Br	2.9278226	-2.9278226	-0.0000000
Br	2.9278226	-0.0000000	-2.9278226
Br	-0.0000000	-0.0000000	-6.2851364
Br	-2.9278226	2.9278226	0.0000000
Br	2.9278226	2.9278226	-0.0000000
Br	-0.0000000	-2.9278226	2.9278226
Br	-2.9278226	-2.9278226	-0.0000000
Br	0.0000000	6.2851364	0.0000000
Br	-2.9278226	0.0000000	2.9278226
Br	0.0000000	0.0000000	0.0000000
Br	0.0000000	2.9278226	2.9278226
Br	-6.2851364	0.0000000	0.0000000
Br	-2.9278226	0.0000000	-2.9278226
Br	0.0000000	2.9278226	-2.9278226
Br	2.9278226	-0.0000000	2.9278226
Br	-0.0000000	-0.0000000	6.2851364

isomer C

La	-1.4384713	-2.4915054	-2.1310571
La	-1.4420484	2.4977011	2.2027002
La	-1.4420484	-2.4977011	2.2027002
La	-1.4384713	2.4915054	-2.1310571
La	2.8840968	0.0000000	2.2027002
La	2.8769426	0.0000000	-2.1310571
Br	-2.5610277	-4.4358301	-3.7404287
Br	-0.0881073	-4.0405192	0.0359742
Br	-3.4551386	2.0965628	0.0359742
Br	-2.4423752	0.0000000	-3.4379310
Br	-2.5599165	4.4339054	3.8245851
Br	1.2193818	-2.1120313	3.5024028
Br	-3.4551386	-2.0965628	0.0359742
Br	-2.5599165	-4.4339054	3.8245851

```
Br   -2.5610277    4.4358301   -3.7404287
Br    0.0000000    0.0000000    0.0222622
Br   -2.4387637    0.0000000    3.5024028
Br   -0.0881073    4.0405192    0.0359742
Br    3.5432459   -1.9439564    0.0359742
Br    3.5432459    1.9439564    0.0359742
Br    1.2211876   -2.1151590   -3.4379310
Br    5.1220555    0.0000000   -3.7404287
Br    1.2211876    2.1151590   -3.4379310
Br    5.1198330    0.0000000    3.8245851
Br    1.2193818    2.1120313    3.5024028
isomer C
Br   -0.0375429    6.2124007    4.3215085
Br   -0.2380876    6.1594108   -3.5766792
Br    0.0000000    0.0000000   -6.5984539
Br    0.2380876   -6.1594108   -3.5766792
Br    0.0375429   -6.2124007    4.3215085
La    0.0601060    4.1423355    2.4672782
La    0.0060048    4.0555208   -1.7891287
La    0.0000000    0.0000000   -3.8419378
La   -0.0060048   -4.0555208   -1.7891287
La   -0.0601060   -4.1423355    2.4672782
Br   -1.9534470    1.9830929   -2.8051710
Br   -0.6260124   -1.7305657    0.3943036
Br   -1.8197600   -5.2712906    0.3053684
Br   -1.7608689   -2.1032352    3.9560197
Br   -1.9990303    4.6841404    0.3516435
Br    1.9990303   -4.6841404    0.3516435
Br    1.9534470   -1.9830929   -2.8051710
Br    0.6260124    1.7305657    0.3943036
Br    1.8197600    5.2712906    0.3053684
Br    1.7608689    2.1032352    3.9560197
Br   -2.0075210    2.0861157    3.3756490
La    0.0000000    0.0000000    2.7488505
Br    2.0075210   -2.0861157    3.3756490
Br   -1.9100438   -2.2359329   -3.2521929
Br    1.9100438    2.2359329   -3.2521929
transition state A-B
La    3.3301511    0.3520668    0.4661474
La   -0.6831128   -0.1860335   -3.5532797
La    0.2199450   -3.4265531   -0.1595133
La   -0.3529009   -0.7166500    4.0560061
La    0.7239089    3.4551672   -1.3978377
La   -2.9299332    0.4583308    0.6748683
Br    0.2674498   -6.1769524   -0.4480806
Br    0.5619753   -2.8291679   -3.1022011
Br    6.0822619    0.5931729    0.5700447
Br    3.1154262   -2.5774156   -0.0165194
Br    2.6887815    1.2575302   -2.3879908
Br   -1.2403748   -0.7939299   -6.1856302
Br   -2.0108848    3.2867128   -0.4037437
Br    2.4403764    3.1725828    0.9939924
Br    0.2679026   -3.3615816    2.8482240
Br   -2.5970679   -2.5767755   -0.2064477
Br    1.2824430    6.0958714   -1.9834807
Br   -3.1306990   -1.2528625    3.2041825
Br    0.1070234   -0.0438416   -0.2788824
Br   -1.1703369    1.8229584    2.8453675
Br   -5.5633379    1.2838006    0.8872864
```

Br	-3.3003966	0.2846342	-2.4412927
Br	-0.2726661	2.6865566	-4.1153526
Br	2.4945398	-0.0542560	3.3083791
Br	-0.3304743	-0.7533649	6.8257541

11. Basis sets lcecp-1-TZVP

```
# bases for f(n-1) ECPs [Theor. Chim. Acta 75, 173 (1989)] ECPs
available from https://www.tc.uni-koeln.de/PP/clickpse.en.html
# bases are optimized for the  s2d1 state at ROHF level; f functions
are interpolated from Theor. Chem. Acc. 126, 117 (2009)
# M. Lukanowski, F. Weigend, manuscript in preparation
*
la lcecp-1-TZVP
# la    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  63.864779023      0.60540168769E-03
  17.902849835      0.11045753215E-02
  7.1557675558     -0.39463206103E-01
  3.5657641010      0.42702922246
   1  s
  2.2607957420       1.0000000000
   1  s
 0.48370757423       1.0000000000
   1  s
 0.22994494416       1.0000000000
   1  s
 0.55862778216E-01   1.0000000000
   1  s
 0.22880457888E-01   1.0000000000
   4  p
  20.588589267      0.82283717125E-03
  7.6900035967     -0.10507314083E-01
  4.0826885418      0.99399166634E-01
  2.2676719740     -0.29416391577
   2  p
 0.61535655867       1.0111652820
 0.30091193143      0.98869814605
   1  p
 0.13789795303       1.0000000000
   1  p
 0.38464309352E-01   1.0000000000
   3  d
  1.3711973377     -0.10688850714
 0.77060387788      0.21163263979
 0.30928785000      0.45115648007
   1  d
 0.12668803845       1.0000000000
   1  d
 0.49019240952E-01   1.0000000000
   1  f
 0.82138400000       1.0000000000
   1  f
 0.29525300000       1.0000000000
*
ce lcecp-1-TZVP
# ce    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  57.732771399      0.65974361681E-03
  19.514407934      0.89004993679E-03
  7.5773318382     -0.41449780107E-01
  3.8218363512      0.42688718438
```

```
   1  s
  2.3637886742       1.0000000000
   1  s
 0.50461229663       1.0000000000
   1  s
 0.23906807850       1.0000000000
   1  s
 0.57378464692E-01   1.0000000000
   1  s
 0.23413442153E-01   1.0000000000
   4  p
  19.205643821      0.91758005989E-03
  8.1036745693     -0.10699281867E-01
  4.3127130736      0.99518746045E-01
  2.3978818419     -0.29389991710
   2  p
 0.64995768299      0.99364679161
 0.31763179414       1.0063115255
   1  p
 0.14540670995       1.0000000000
   1  p
 0.40599047410E-01   1.0000000000
   3  d
  1.4879717238     -0.92840135170E-01
 0.79683615085      0.20331174230
 0.32322243721      0.44470243479
   1  d
 0.13170292973       1.0000000000
   1  d
 0.50516339833E-01   1.0000000000
   1  f
 0.85188700000       1.0000000000
   1  f
 0.32041900000       1.0000000000
*
pr lcecp-1-TZVP
# pr    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  29.816069324     -0.89180920206E-04
  21.166653138      0.38272921102E-02
  9.0081480723     -0.41246744060E-01
  4.2392154015      0.35771383679
   1  s
  2.4241845947       1.0000000000
   1  s
 0.53433804194       1.0000000000
   1  s
 0.25402869128       1.0000000000
   1  s
 0.58750331139E-01   1.0000000000
   1  s
 0.23943357104E-01   1.0000000000
   4  p
  16.564476747      0.84759630880E-03
  7.9529419731     -0.10455162210E-01
  4.4233492341      0.99298780032E-01
  2.4946852254     -0.29431394490
   2  p
```

```
 0.73046985081      0.86756674483
 0.36876667442       1.1169106818
   1  p
 0.17024053688       1.0000000000
   1  p
 0.50095330022E-01   1.0000000000
   3  d
  1.6236670955     -0.79428546412E-01
 0.80699533694      0.20078239067
 0.33101487572      0.44068002536
   1  d
 0.13452470163       1.0000000000
   1  d
 0.51298503030E-01   1.0000000000
   1  f
 0.85188700000       1.0000000000
   1  f
 0.32041900000       1.0000000000
*
nd lcecp-1-TZVP
# nd    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  27.763855481     -0.47425674935E-03
  24.134743379      0.33878701606E-02
  9.2665348546     -0.43685546953E-01
  4.3760727574      0.42298961855
   1  s
  2.5983493665       1.0000000000
   1  s
 0.55342477699       1.0000000000
   1  s
 0.26108203546       1.0000000000
   1  s
 0.60814203933E-01   1.0000000000
   1  s
 0.24619092767E-01   1.0000000000
   4  p
  19.443514810      0.93330575892E-03
  8.8689560924     -0.10728737034E-01
  4.7726721487      0.99374679398E-01
  2.6630476779     -0.29336677298
   2  p
 0.72433715387      0.94928634025
 0.35879388280       1.0482618507
   1  p
 0.16795780796       1.0000000000
   1  p
 0.54608884705E-01   1.0000000000
   3  d
  1.7242596801     -0.75107605717E-01
 0.85330125778      0.19417965302
 0.34885799385      0.43422320954
   1  d
 0.14037401203       1.0000000000
   1  d
 0.52873106884E-01   1.0000000000
   1  f
 0.86220500000       1.0000000000
```

```
   1  f
 0.32315800000       1.0000000000
*
pm lcecp-1-TZVP
# pm    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  35.383914046      0.15598959103E-04
  24.569476887      0.25998174846E-02
  9.6058760699     -0.45030340637E-01
  4.6078668362      0.43144020001
   1  s
  2.7437104259       1.0000000000
   1  s
 0.57271069098       1.0000000000
   1  s
 0.26808248232       1.0000000000
   1  s
 0.62758775387E-01   1.0000000000
   1  s
 0.25256848108E-01   1.0000000000
   4  p
  19.660271607      0.94836944219E-03
  9.3394872970     -0.10746508606E-01
  5.0251403397      0.99368198849E-01
  2.8025170101     -0.29336314583
   2  p
 0.75861206032      0.93459492100
 0.37243676843       1.0613713134
   1  p
 0.17096770996       1.0000000000
   1  p
 0.50510566032E-01   1.0000000000
   3  d
  1.8618737711     -0.66142585397E-01
 0.87328021918      0.19166840460
 0.35850558890      0.42925390965
   1  d
 0.14359214848       1.0000000000
   1  d
 0.53689060406E-01   1.0000000000
   1  f
 0.86248300000       1.0000000000
   1  f
 0.32129300000       1.0000000000
*
sm lcecp-1-TZVP
# sm    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  37.145664287      0.13385971234E-03
  25.368169880      0.25409081468E-02
  10.216779829     -0.45788164251E-01
  4.8685967188      0.43758465910
   1  s
  2.8826786703       1.0000000000
   1  s
 0.59607355877       1.0000000000
   1  s
```

```
 0.27852160387       1.0000000000
   1  s
 0.64495822101E-01   1.0000000000
   1  s
 0.25857756051E-01   1.0000000000
   4  p
  20.039579623      0.95072915997E-03
  9.8566823430     -0.10746723002E-01
  5.2962287476      0.99368143878E-01
  2.9495187405     -0.29336321639
   2  p
 0.78803582181      0.93535242299
 0.38217489886       1.0702663020
   1  p
 0.17197390469       1.0000000000
   1  p
 0.44741227869E-01   1.0000000000
   3  d
  2.0090735197     -0.58367247502E-01
 0.88829265378      0.19202824467
 0.36543002086      0.42557783483
   1  d
 0.14548852027       1.0000000000
   1  d
 0.54005822675E-01   1.0000000000
   1  f
 0.89259700000       1.0000000000
   1  f
 0.33084900000       1.0000000000
*
eu lcecp-1-TZVP
# eu    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  34.846677897      0.10219369590E-02
  27.048529555      0.11913213776E-02
  10.884836755     -0.42400565227E-01
  5.2262668302      0.40055102341
   1  s
  2.9776698362       1.0000000000
   1  s
 0.61984210700       1.0000000000
   1  s
 0.28940552156       1.0000000000
   1  s
 0.66120587896E-01   1.0000000000
   1  s
 0.26432815618E-01   1.0000000000
   4  p
  33.778015990      0.10746666174E-02
  14.352595249     -0.69157410916E-02
  5.8479813026      0.10407328347
  2.9833910027     -0.41441223487
   2  p
 0.83643041905      0.90427967752
 0.40345975394       1.0966403546
   1  p
 0.18027234924       1.0000000000
   1  p
```

```
 0.46435676918E-01   1.0000000000
   3  d
  2.1866773802     -0.49243138011E-01
 0.89942817342      0.19420448526
 0.37064451504      0.42192647155
   1  d
 0.14677017936       1.0000000000
   1  d
 0.54137917652E-01   1.0000000000
   1  f
 0.91528700000       1.0000000000
   1  f
 0.33269300000       1.0000000000
*
gd lcecp-1-TZVP
# gd    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  38.065819271      0.65913677181E-03
  22.184792246      0.23555350310E-02
  11.393164980     -0.43999232242E-01
  5.4713762850      0.39762999373
   1  s
  3.1790607778       1.0000000000
   1  s
 0.63993871371       1.0000000000
   1  s
 0.29435311227       1.0000000000
   1  s
 0.68826280495E-01   1.0000000000
   1  s
 0.27257576420E-01   1.0000000000
   4  p
  36.424317213      0.89706054909E-03
  13.806682936     -0.63896425772E-02
  6.1207357653      0.10335011637
  3.1792850722     -0.41480315344
   2  p
 0.84590034316      0.92915703819
 0.40335900243       1.0756697691
   1  p
 0.17869725595       1.0000000000
   1  p
 0.43768369641E-01   1.0000000000
   3  d
  2.4402128428     -0.30335642216E-01
 0.90109978094      0.19837175954
 0.37254934356      0.41769331268
   1  d
 0.14704901553       1.0000000000
   1  d
 0.54008723557E-01   1.0000000000
   1  f
 0.98368500000       1.0000000000
   1  f
 0.35716600000       1.0000000000
*
tb lcecp-1-TZVP
# tb    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
```

```
*
   4  s
  40.333832878      0.12274726691E-02
  26.752982055      0.80768975368E-03
  12.194036601     -0.42292627261E-01
  5.8489378874      0.40025278415
   1  s
  3.2720640831       1.0000000000
   1  s
 0.66730324910       1.0000000000
   1  s
 0.30924546034       1.0000000000
   1  s
 0.70067705568E-01   1.0000000000
   1  s
 0.27762265684E-01   1.0000000000
   4  p
  39.758681778      0.83110416803E-03
  13.942746782     -0.61424201656E-02
  6.4420335703      0.10300352741
  3.3722338254     -0.41509711721
   2  p
 0.86776767593      0.94164695531
 0.41055009999       1.0645575743
   1  p
 0.18143127871       1.0000000000
   1  p
 0.44587546979E-01   1.0000000000
   3  d
  2.6075843147     -0.29342538394E-01
 0.93378947333      0.19789560630
 0.38105114407      0.41725087511
   1  d
 0.14801128959       1.0000000000
   1  d
 0.53532783909E-01   1.0000000000
   1  f
  1.0132660000       1.0000000000
   1  f
 0.36508100000       1.0000000000
*
dy lcecp-1-TZVP
# dy    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  42.039522958      0.19267097163E-02
  18.100659230     -0.87342740858E-03
  13.039591354     -0.41279953549E-01
  6.2572988865      0.40647306865
   1  s
  3.3765707524       1.0000000000
   1  s
 0.69178753741       1.0000000000
   1  s
 0.32013414557       1.0000000000
   1  s
 0.71848395130E-01   1.0000000000
   1  s
 0.28384464287E-01   1.0000000000
```

```
   4  p
  41.972734598      0.78670841484E-03
  13.917660437     -0.59457009603E-02
  6.7311224620      0.10270273457
  3.5555414202     -0.41533894142
   2  p
 0.90321607482      0.93305189756
 0.42872081935       1.0721240758
   1  p
 0.19138003417       1.0000000000
   1  p
 0.52289337994E-01   1.0000000000
   3  d
  2.8364090549     -0.24549505777E-01
 0.95784135316      0.19904322139
 0.38836911079      0.41229318624
   1  d
 0.15035223573       1.0000000000
   1  d
 0.54185564514E-01   1.0000000000
   1  f
  1.0377460000       1.0000000000
   1  f
 0.36716500000       1.0000000000
*
ho lcecp-1-TZVP
# ho    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  41.366233170      0.27604491279E-02
  16.763685225     -0.40136357545E-02
  14.458392963     -0.37057116927E-01
  6.7116441958      0.40614136694
   1  s
  3.4774056194       1.0000000000
   1  s
 0.71724607315       1.0000000000
   1  s
 0.33110277512       1.0000000000
   1  s
 0.73689390385E-01   1.0000000000
   1  s
 0.29013015307E-01   1.0000000000
   4  p
  40.264189634      0.78561322985E-03
  13.243541249     -0.59536510489E-02
  6.9994754573      0.10270417955
  3.7467137579     -0.41533860758
   2  p
 0.93673864182      0.92736352200
 0.44336119439       1.0772016731
   1  p
 0.19745596463       1.0000000000
   1  p
 0.54002963528E-01   1.0000000000
   3  d
  3.0360072126     -0.23374291513E-01
 0.99203732539      0.19788118114
 0.39779225255      0.40921856488
```

```
   1  d
 0.15233627532       1.0000000000
   1  d
 0.54277692708E-01   1.0000000000
   1  f
  1.0730650000       1.0000000000
   1  f
 0.37740000000       1.0000000000
*
er lcecp-1-TZVP
# er    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  38.065269306      0.51275207503E-02
  18.135753575     -0.10641143486E-01
  16.846883883     -0.28468494744E-01
  7.1712675526      0.40482115229
   1  s
  3.5830906524       1.0000000000
   1  s
 0.74386875334       1.0000000000
   1  s
 0.34298856877       1.0000000000
   1  s
 0.75556697864E-01   1.0000000000
   1  s
 0.29674684060E-01   1.0000000000
   4  p
  44.533641855      0.76389302440E-03
  12.668583462     -0.59207521659E-02
  7.2973749933      0.10269752833
  3.9535941169     -0.41536044234
   2  p
 0.96342834698      0.93220150717
 0.45155303769       1.0728333300
   1  p
 0.19916727549       1.0000000000
   1  p
 0.51813337946E-01   1.0000000000
   3  d
  3.2148454534     -0.24148250497E-01
  1.0334089353      0.19461633437
 0.41022966910      0.40471986646
   1  d
 0.15540888218       1.0000000000
   1  d
 0.54684041031E-01   1.0000000000
   1  f
  1.1102730000       1.0000000000
   1  f
 0.38808200000       1.0000000000
*
tm lcecp-1-TZVP
# tm    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  37.611504755      0.83225787245E-02
  21.166525800     -0.19033133292E-01
  19.412348059     -0.17884911925E-01
```

```
  7.5798341321      0.40463645763
   1  s
  3.7099736488       1.0000000000
   1  s
 0.76802947715       1.0000000000
   1  s
 0.35242240785       1.0000000000
   1  s
 0.77597477473E-01   1.0000000000
   1  s
 0.30354109359E-01   1.0000000000
   4  p
  45.652350627      0.69521603819E-03
  11.923103269     -0.55370262098E-02
  7.5487987872      0.10212202329
  4.1462031016     -0.41525637260
   2  p
  1.0047875604      0.92031879504
 0.47261346579       1.0836438326
   1  p
 0.21028382917       1.0000000000
   1  p
 0.59593473102E-01   1.0000000000
   3  d
  3.5151898589     -0.17713573535E-01
  1.0707940133      0.19234267576
 0.42053137594      0.40056103676
   1  d
 0.15754633865       1.0000000000
   1  d
 0.54773162482E-01   1.0000000000
   1  f
  1.1517430000       1.0000000000
   1  f
 0.40078400000       1.0000000000
*
yb lcecp-1-TZVP
# yb    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  38.980310756      0.14221522013E-01
  26.373948359     -0.32543225887E-01
  14.248841675     -0.34428797749E-03
  7.7840898690      0.40132229256
   1  s
  3.8744796438       1.0000000000
   1  s
 0.79035049428       1.0000000000
   1  s
 0.36135022278       1.0000000000
   1  s
 0.79788595812E-01   1.0000000000
   1  s
 0.31079360000E-01   1.0000000000
   4  p
  54.301315594      0.76725539439E-03
  11.100902367     -0.87804758139E-02
  8.2786431270      0.94999039462E-01
  4.2908832507     -0.42863242384
```

```
   2  p
  1.0351654372      0.92063596803
 0.48165600896       1.0831089662
   1  p
 0.21119386036       1.0000000000
   1  p
 0.54795290601E-01   1.0000000000
   3  d
  3.6979927180     -0.20893060765E-01
  1.1089131984      0.19078779810
 0.42994646755      0.39742320904
   1  d
 0.15908102453       1.0000000000
   1  d
 0.54610561138E-01   1.0000000000
   1  f
  1.1983260000       1.0000000000
   1  f
 0.41814000000       1.0000000000
*
lu lcecp-1-TZVP
# lu    (9s8p5d2f) / [6s4p3d2f]     {411111/4211/311/11}
*
   4  s
  40.883824190      0.17258662678E-01
  27.779820125     -0.38645315738E-01
  9.7131380125      0.10002864275E-01
  8.5119139923      0.38802370076
   1  s
  3.9653033156       1.0000000000
   1  s
 0.82137709788       1.0000000000
   1  s
 0.37594982026       1.0000000000
   1  s
 0.81676957820E-01   1.0000000000
   1  s
 0.31775814404E-01   1.0000000000
   4  p
  56.714902481      0.96964336280E-03
  20.524912681     -0.77768201557E-03
  8.5357140387      0.85923200711E-01
  4.4899206738     -0.44279410778
   2  p
  1.0676118697      0.92099412383
 0.49112714468       1.0826517653
   1  p
 0.21250749794       1.0000000000
   1  p
 0.50677363582E-01   1.0000000000
   3  d
  3.9646561111     -0.19718415679E-01
  1.1494558674      0.18845542585
 0.44003928786      0.39351076652
   1  d
 0.16077765999       1.0000000000
   1  d
 0.54467426998E-01   1.0000000000
   1  f
```

```
  1.0055160000       1.0000000000
   1   f
 0.37082800000       1.0000000000
*
$end
```

12. 28-mwb 3s3p1d basis set and effective core potential

```
$basis
br 28-mwb 3s3p1d
# M. Dolg, PhD-thesis, Stuttgart, 1989
*
  4  s
  150.60174      .14565000E-02
  4.8291220      .41246150
  2.2103710     -1.8094733
  .50716200      .93823000
  1  s
  .32604300      1.0000000
  1  s
  .12027500      1.0000000
  4  p
  41.713235      .18770000E-03
  5.2609120      .70722500E-01
  2.7140910     -.39092940
  .59447200      1.1429490
  1  p
  .23039300      1.0000000
  1  p
  .72212000E-01  1.0000000
  1  d
  .38900000      1.0000000
*
$ecp
*
    ncore = 28    lmax = 3
f
   -8.16149293    2    2.7207
s-f
   61.51372099    2    5.0218
    9.02149299    2    2.5109
p-f
   53.87586402    2    4.2814
    4.62940227    2    2.1407
d-f
   20.84967744    2    2.8800
    2.96544431    2    1.4400
*
$end
```