Supplementary Information for:

Composite ab initio vibrational spectroscopy and thermochemistry of low-valency lanthanide compounds: europium dihalides EuX_2 (X = F, Cl, Br, I)

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Includes 16 tables and 1 Figure providing:

- anharmonic corrections to vibrational frequencies of EuX_2 at the MP2 and CCSD(T) levels of theory
- infrared intensities of EuX_2
- gas-phase extrapolations of the stretching fundamentals of matrix-isolated EuF_2 and $EuCl_2$
- calculated and experimental isotopic shifts in bond stretching vibrational frequencies of $EuCl_2$ and $EuBr_2$
- the ground state second-order spin-orbit splittings in EuX_2 and EuX
- force constants of EuX and EuX_2 in natural (valence) coordinates
- thermal functions in the 298.15–1600 K temperature range for the gaseous EuX_2 species (X = F, Cl, Br, I) obtained using the geometries and vibrational frequencies calculated at the CCSD(T)/CBS level of theory. Statistical weight = 8, symmetry number = 2.
- thermal functions in the 298.15–1600 K temperature range for the gaseous EuX species (X = F, Cl, Br, I) obtained using the bond length and vibrational frequencies calculated at the CCSD(T)/CBS level of theory. Statistical weight = 9, symmetry number = 1.

  Units in Tables S7–S14 are as follows:

  $\mathbf{C_p}$, **S**, **Φ** = S(T) – [H(T)–H(0)]/T, **G** = S(T) – [(H(T)–H(298)]/T – cal/(mol·K); **H(T)–H(0)** – cal/mol.
- pseudopotential-based results for bond lengths, bond angles, barriers to linearity, bond length differences between the linear and bent geometries, harmonic vibrational frequencies, and atomization energies of europium dihalides EuX_2, as determined at the MP2 and CCSD(T) levels of theory
- correlation between bond dissociation (EuX) or bond cleavage (EuX_2) energies and bond-stretching force constants in EuX and EuX_2

Table S1 MP2/LPP and CCSD(T)/LPP calculated anharmonic corrections to the vibrational frequencies of EuX_2, cm^{-1}

		$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$
EuF_2	MP2	–3.9	–1.3	–3.9
	CCSD(T)	–3.9	–1.5	–3.7
$EuCl_2$	MP2	–1.8	–0.5	–1.7
	CCSD(T)	–1.8	–0.6	–1.7
$EuBr_2$	MP2	–1.0	0.0	–0.8
	CCSD(T)	–1.1	0.0	–0.8
EuI_2	MP2	–0.9	0.5	–0.5
	CCSD(T)	–0.9	0.5	–0.4

Table S2 Infrared intensities A_i (km/mol) of the harmonic and fundamental (in *italic*) vibrational transitions in EuX_2

	Level	A_1	A_2	A_3
EuF_2	MP2/LPP	48.8	36.2	222.1
		51.5	*48.6*	*217.0*
	HF/QZ	69.0	31.2	211.3
	CCSD(T)/TZ	63.0	23.5	208.9
$EuCl_2$	MP2/LPP	11.9	24.7	130.4
		12.3	*38.0*	*127.2*
	HF/QZ	18.7	21.2	121.7
	CCSD(T)/TZ	16.4	17.6	119.6
$EuBr_2$	MP2/LPP	5.5	14.3	78.2
		5.7	*22.5*	*75.1*
	HF/QZ	9.6	11.7	71.4
	CCSD(T)/TZ	8.2	9.7	70.4
EuI_2	MP2/LPP	2.3	11.6	63.0
		2.2	*18.1*	*59.1*
	HF/QZ	5.6	9.0	56.2
	CCSD(T)/TZ	4.7	7.5	55.8

Table S3 Gas-phase extrapolations of the stretching fundamentals of matrix-isolated EuF_2 and $EuCl_2$ (see also Table 3 of the main text)

	EuF_2		$EuCl_2$	
	ν_1	ν_3	ν_1	ν_3
Two-point (Ne–Ar) linear extrapolation to zero polarizability[a]	479	457	278	289
Three-point (Ne–Ar–Kr) linear extrapolation to zero polarizability[a]			279	291

[a] Ne, Ar, and Kr polarizabilities, 0.394, 1.641 and 2.484 $Å^3$, respectively, are taken from E. John R. Rumble, CRC Handbook of Chemistry and Physics, 99th Edition, CRC Press/Taylor & Francis, 2018 (Internet Version 2018).

Table S4 Theoretical and experimental isotopic shifts, cm^{-1}, in bond stretching vibrational frequencies of $EuCl_2$ and $EuBr_2$ relative to $^{37}Cl–^{37}Cl$ and $^{81}Br–^{81}Br$, respectively

	$EuCl_2$		$EuBr_2$	
	$^{35}Cl–^{35}Cl$	$^{35}Cl–^{37}Cl$	$^{79}Br–^{79}Br$	$^{79}Br–^{81}Br$
$\Delta\omega_1$(theory)	7.07	2.63	1.91	1.41
$\Delta\omega_3$(theory)	5.83	3.82	0.93	0.73
$\Delta\nu_3$(theory)[a]	5.1	3.4		
$\Delta\nu_3$(MI, N_2)	4.9 (HHM)	3.2 (HHM)		
	5.0 (DWR)	3.4 (DWR)		

[a] The values of $\Delta\nu_3$(theory) were obtained by scaling $\Delta\omega_3$(theory) for a nitrogen matrix effect with the formula $\Delta\nu_3$(theory) = $\Delta\omega_3$(theory) × ν_3(MI, N_2) / ν_3(theory) using the ν_3(MI, N_2) values reported by HHM and DWR for $EuCl_2$

Table S5 4c-AoC-SCF calculated second-order spin–orbit splittings, cm^{-1}, in the electronic ground states of EuX_2

Level (degeneracy)	EuF_2	$EuCl_2$	$EuBr_2$	EuI_2
1 (2)	0.0	0.0	0.0	0.0
2 (2)	3.4	2.5	3.2	4.5
3 (2)	5.7	4.2	5.4	7.5
4 (2)	6.9	5.0	6.6	9.2

Table S6 4c-AoC-SCF calculated second-order spin–orbit splittings, cm^{-1}, in the electronic ground states of EuX

Level (degeneracy)	EuF	EuCl	EuBr	EuI
1 (1)	0.00	0.00	0.00	0.00
2 (2)	0.12	0.09	0.01	0.04
3 (2)	0.48	0.37	0.06	0.17
4 (2)	1.05	0.83	0.13	0.39
5 (2)	1.79	1.44	0.23	0.70

Table S7 CCSD(T)/CBS calculated force constants of EuX and EuX_2 in natural coordinates. Units are mdyn·$Å^{-1}$ for f_r and f_{rr}, mdyn·Å for f_α, and mdyn for $f_{r\alpha}$

	EuX	EuX_2			
X	f_r	f_r	f_{rr}	$f_{r\alpha}$	f_α
F	2.4564	2.2550	0.1945	–0.2815	0.8835
Cl	1.4009	1.4034	0.1082	–0.1682	0.4298
Br	1.1973	1.2257	0.0902	–0.1406	0.3330
I	0.9573	0.9951	0.0741	–0.1025	0.2071

Table S8 Thermal functions for gaseous EuF_2

T	C_p	S	Φ	G	H(T)–H(0)
298.15	12.495	74.224	63.726	74.224	3129.978
300	12.509	74.301	63.791	74.224	3153.107
400	13.039	77.981	66.897	74.722	4433.420
500	13.325	80.924	69.418	75.678	5753.008
600	13.493	83.370	71.545	76.762	7094.600
700	13.598	85.458	73.387	77.859	8449.546
800	13.669	87.279	75.012	78.925	9813.140
900	13.718	88.892	76.467	79.944	11182.634
1000	13.754	90.339	77.783	80.913	12556.323
1100	13.780	91.651	78.985	81.830	13933.096
1200	13.801	92.851	80.091	82.699	15312.201
1300	13.817	93.957	81.116	83.523	16693.112
1400	13.829	94.981	82.070	84.306	18075.449
1500	13.840	95.936	82.963	85.050	19458.930
1600	13.848	96.829	83.802	85.758	20843.343

Table S9 Thermal functions for gaseous $EuCl_2$

T	C_p	S	Φ	G	H(T)–H(0)
298.15	13.315	80.432	68.882	80.432	3443.669
300	13.322	80.514	68.953	80.432	3468.308
400	13.566	84.385	72.349	80.958	4814.271
500	13.686	87.426	75.071	81.959	6177.467
600	13.753	89.928	77.345	83.085	7549.669
700	13.794	92.051	79.298	84.218	8927.136
800	13.821	93.895	81.010	85.315	10307.938
900	13.839	95.524	82.534	86.360	11690.983
1000	13.853	96.983	83.907	87.351	13075.607
1100	13.862	98.303	85.157	88.287	14461.384
1200	13.870	99.510	86.303	89.173	15848.029
1300	13.876	100.620	87.363	90.011	17235.343
1400	13.881	101.649	88.347	90.806	18623.183
1500	13.884	102.607	89.266	91.562	20011.444
1600	13.888	103.503	90.128	92.280	21400.049

Table S10 Thermal functions for gaseous $EuBr_2$

T	C_p	S	Φ	G	H(T)–H(0)
298.15	13.614	85.974	73.804	85.974	3628.499
300	13.618	86.058	73.879	85.974	3653.688
400	13.742	89.995	77.439	86.510	5022.532
500	13.802	93.069	80.269	87.526	6400.054
600	13.834	95.589	82.619	88.666	7782.010
700	13.854	97.723	84.628	89.811	9166.529
800	13.867	99.574	86.383	90.918	10552.660
900	13.876	101.208	87.941	91.973	11939.870
1000	13.883	102.670	89.342	92.971	13327.838
1100	13.887	103.993	90.615	93.913	14716.358
1200	13.891	105.202	91.781	94.805	16105.293
1300	13.894	106.314	92.856	95.648	17494.547
1400	13.896	107.344	93.855	96.447	18884.053
1500	13.898	108.302	94.787	97.206	20273.759
1600	13.899	109.199	95.660	97.927	21663.629

Table S11 Thermal functions for gaseous EuI_2

T	C_p	S	Φ	G	H(T)–H(0)
298.15	13.729	89.963	77.430	89.963	3736.790
300	13.731	90.048	77.508	89.964	3762.191
400	13.808	94.011	81.161	90.503	5139.694
500	13.845	97.096	84.051	91.525	6522.528
600	13.864	99.622	86.442	92.670	7908.065
700	13.876	101.760	88.482	93.820	9295.158
800	13.884	103.614	90.260	94.931	10683.226
900	13.890	105.250	91.836	95.988	12071.947
1000	13.894	106.713	93.252	96.989	13461.126
1100	13.896	108.038	94.537	97.934	14850.639
1200	13.899	109.247	95.713	98.827	16240.401
1300	13.900	110.359	96.798	99.672	17630.356
1400	13.902	111.390	97.804	100.473	19020.462
1500	13.903	112.349	98.742	101.233	20410.689
1600	13.904	113.246	99.620	101.956	21801.015

Table S12 Thermal functions for gaseous EuF

T	C_p	S	Φ	G	H(T)–H(0)
298.15	8.212	61.843	54.411	61.843	2215.820
300	8.219	61.894	54.457	61.843	2231.019
400	8.488	64.299	56.630	62.169	3067.817
500	8.636	66.211	58.361	62.793	3924.719
600	8.723	67.793	59.805	63.498	4793.021
700	8.778	69.143	61.045	64.210	5668.285
800	8.815	70.317	62.132	64.902	6548.075
900	8.841	71.357	63.101	65.563	7430.961
1000	8.860	72.290	63.974	66.189	8316.050
1100	8.874	73.135	64.769	66.783	9202.762
1200	8.885	73.907	65.498	67.345	10090.702
1300	8.893	74.619	66.173	67.878	10979.593
1400	8.900	75.278	66.800	68.383	11869.236
1500	8.905	75.892	67.386	68.863	12759.481
1600	8.910	76.467	67.936	69.321	13650.220

Table S13 Thermal functions for gaseous EuCl

T	C_p	S	Φ	G	H(T)–H(0)
298.15	8.649	64.831	56.963	64.831	2346.044
300	8.652	64.885	57.011	64.831	2362.048
400	8.773	67.393	59.307	65.173	3234.079
500	8.832	69.357	61.128	65.820	4114.596
600	8.865	70.971	62.638	66.548	4999.548
700	8.885	72.339	63.929	67.280	5887.095
800	8.898	73.526	65.056	67.988	6776.286
900	8.907	74.575	66.056	68.663	7666.581
1000	8.914	75.513	66.956	69.302	8557.655
1100	8.919	76.363	67.773	69.906	9449.297
1200	8.922	77.140	68.522	70.477	10341.367
1300	8.925	77.854	69.212	71.017	11233.767
1400	8.928	78.515	69.854	71.529	12126.426
1500	8.930	79.131	70.452	72.016	13019.293
1600	8.931	79.708	71.013	72.479	13912.329

Table S14 Thermal functions for gaseous EuBr

T	C_p	S	Φ	G	H(T)–H(0)
298.15	8.798	67.562	59.419	67.562	2427.879
300	8.800	67.616	59.469	67.562	2444.157
400	8.861	70.158	61.839	67.908	3327.603
500	8.890	72.138	63.708	68.563	4215.271
600	8.905	73.760	65.252	69.298	5105.094
700	8.915	75.134	66.568	70.036	5996.162
800	8.921	76.325	67.715	70.750	6888.014
900	8.926	77.376	68.731	71.429	7780.390
1000	8.929	78.317	69.643	72.071	8673.134
1100	8.931	79.168	70.471	72.678	9566.147
1200	8.933	79.945	71.229	73.252	10459.360
1300	8.934	80.660	71.927	73.795	11352.729
1400	8.935	81.322	72.575	74.309	12246.220
1500	8.936	81.939	73.179	74.797	13139.809
1600	8.937	82.515	73.744	75.262	14033.477

Table S15 Thermal functions for gaseous EuI

T	C_p	S	Φ	G	H(T)–H(0)
298.15	8.854	69.474	61.177	69.474	2473.974
300	8.855	69.529	61.228	69.475	2490.356
400	8.893	72.083	63.638	69.823	3378.021
500	8.910	74.069	65.533	70.481	4268.278
600	8.920	75.695	67.095	71.218	5159.846
700	8.926	77.070	68.424	71.958	6052.168
800	8.930	78.262	69.581	72.674	6944.964
900	8.932	79.314	70.605	73.354	7838.077
1000	8.934	80.255	71.524	73.998	8731.411
1100	8.936	81.107	72.357	74.606	9624.907
1200	8.937	81.885	73.119	75.181	10518.524
1300	8.937	82.600	73.821	75.724	11412.234
1400	8.938	83.262	74.472	76.239	12306.018
1500	8.939	83.879	75.079	76.728	13199.861
1600	8.939	84.456	75.647	77.194	14093.751

Table S16 Bond lengths r_e, Å, bond angles α_e, deg., barriers to linearity h, cm^{-1}, bond length differences between the linear and bent geometries Δr_b, Å, harmonic vibrational frequencies ω_i, cm^{-1}, and total atomization energies TAE, $kcal \cdot mol^{-1}$, of the europium dihalides EuX_2 (X = F, Cl, Br, I)

		r_e	α_e	h	Δr_b	ω_1	ω_2	ω_3	TAE
EuF_2									
MP2	LPP	2.148	126.0	1181	0.046	462	89	440	274
	LPP+CPP	2.132	124.5	1307	0.047	474	86	451	277
	SPP	2.118	117.9	2023	0.060	481	102	458	275
	TZ	2.118	116.9	2136	0.062	481	102	459	275
CCSD(T)	LPP	2.149	126.2	1154	0.045	463	89	442	258
	LPP+CPP	2.134	124.8	1267	0.045	472	91	449	258
	SPP	2.126	118.9	1882	0.057	479	99	458	259
	TZ	2.126	118.5	1969	0.058	479	100	458	259
$EuCl_2$									
MP2	LPP	2.638	139.9	240	0.024	272	37	283	210
	LPP+CPP	2.625	138.5	270	0.025	279	33	290	211
	SPP	2.586	130.7	547	0.035	285	45	296	212
	TZ	2.587	129.6	639	0.037	285	46	295	211
CCSD(T)	LPP	2.650	141.3	207	0.022	268	36	280	202
	LPP+CPP	2.631	139.2	254	0.024	273	38	284	201
	SPP	2.607	133.3	446	0.031	280	42	291	204
	TZ	2.608	131.7	521	0.033	279	44	290	203
$EuBr_2$									
MP2	LPP	2.794	145.4	124	0.017	172	22	207	180
	LPP+CPP	2.782	144.3	138	0.018	177	19	212	180
	SPP/LPP	2.737	133.9	344	0.030	184	28	215	182
	SPP/SPP	2.729	134.7	367	0.028	184	28	216	184
	TZ	2.729	132.6	452	0.032	186	31	216	184
CCSD(T)	LPP	2.809	147.5	99	0.015	169	21	205	174
	LPP+CPP	2.790	145.1	127	0.017	173	22	207	173
	SPP/LPP	2.761	137.3	263	0.025	178	26	211	176
	SPP/SPP	2.754	137.2	274	0.025	179	26	212	177
	TZ	2.757	135.3	343	0.027	180	28	212	177
EuI_2									
MP2	LPP	3.033	156.0	26	0.008	122	13	172	145
	LPP+CPP	3.023	154.9	30	0.008	125	9	175	145
	SPP/LPP	2.966	140.4	139	0.021	134	18	178	147
	SPP/SPP	2.949	141.1	177	0.020	134	18	179	150
	TZ	2.948	136.9	255	0.025	127	32	183	150
CCSD(T)	LPP	3.050	159.2	15	0.006	119	12	170	139
	LPP+CPP	3.030	156.0	26	0.008	122	13	172	138
	SPP/LPP	2.993	145.9	90	0.015	128	16	174	141
	SPP/SPP	2.980	144.5	108	0.016	129	17	175	143
	TZ	2.982	141.4	168	0.020	131	19	173	143

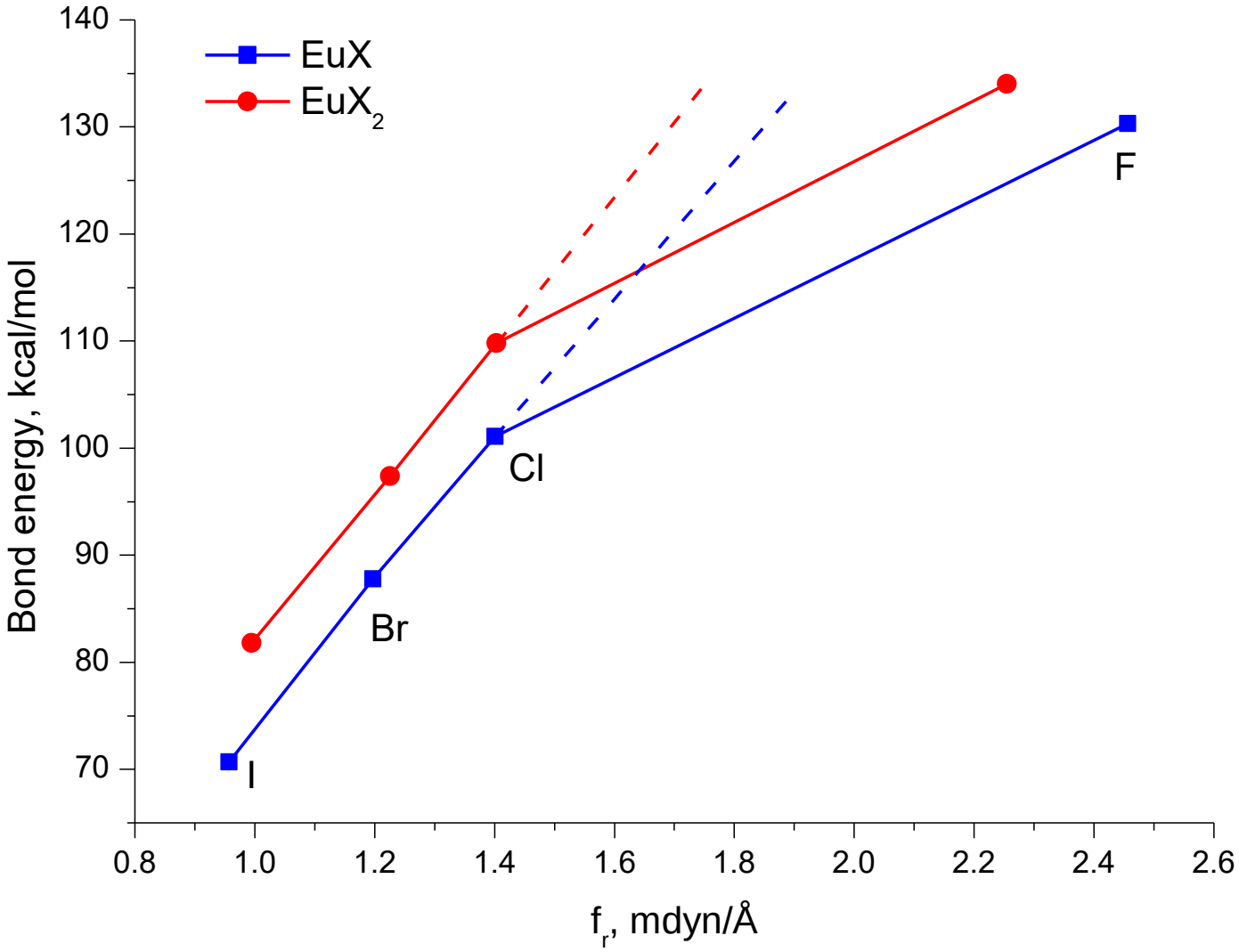

Fig. S1 Bond dissociation ($EuX \rightarrow Eu + X$) and bond cleavage ($EuX_2 \rightarrow EuX + X$) energies vs. bond-stretching force constants in EuX and EuX_2