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Towards a Rational Design of Laser-Coolable Molecules: Insights from Equation-of-Motion Coupled-Cluster Calculations: Supporting Information

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This document contains a detailed summary of the results from EOM-CC calculations (Dyson orbitals, equilibrium bond lengths, excitation energies, oscillator strengths), their comparison with available experimental data, and quantum defects data.

1. EOM-CC CALCULATIONS

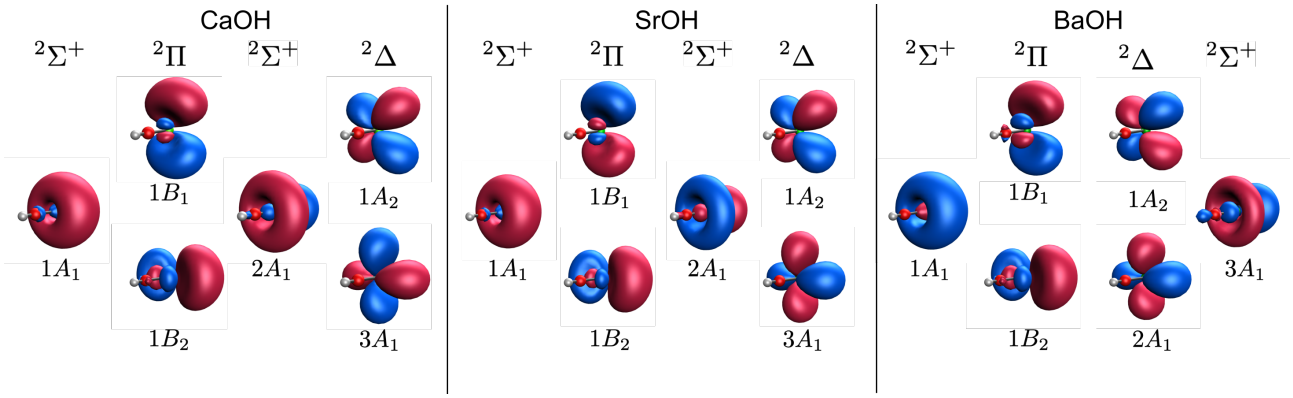

FIG. S1: Dyson orbitals of CaOH, SrOH and BaOH (isovalue = 0.02).

TABLE S1: Comparison between the experimental T_e value and adiabatic (E_{ex}^{ad}) and vertical (E_{ex}^{vert}) excitation energies (in eV) computed using EOM-EA-CCSD. The experimental values for MF and MOH are from Refs. 1 2, respectively.

Molecule		$X^2\Sigma^+ \rightarrow A^2\Pi$				$X^2\Sigma^+ \rightarrow B^2\Sigma^+$		
M	R	$T_e[A^2_{1/2}]$	$T_e[A^2_{3/2}]$	E_{ex}^{ad}	E_{ex}^{vert}	T_e	E_{ex}^{ad}	E_{ex}^{vert}
Ca	F	2.044	2.053	2.097	2.100	2.336	2.436	2.437
	OH	1.979	1.988	2.027	2.034	2.234	2.336	2.341
Sr	F	1.868	1.903	1.903	1.905	2.141	2.179	2.179
	OH	1.803	1.836	1.830	1.835	2.030	2.066	2.069
Ba	F	1.444	1.522	1.510	1.511	1.744	1.754	1.765
	OH	1.435	1.513	1.471	1.471	1.637	1.639	1.642

TABLE S2: Comparison of the equilibrium bond lengths (in Å) calculated using EOM-EA-CCSD with the available experimental values (r_0 and r_e).

Molecule	Bond Length	$X^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$	$X^2\Sigma^+ - A^2\Pi$	$X^2\Sigma^+ - B^2\Sigma^+$
CaF	calc.	1.966	1.947	1.961	-0.019	-0.005
	r_e(Ref. 1)	1.967	1.952	1.955	-0.015	-0.012
CaOH	calc.	1.988	1.962	1.964	-0.026	-0.024
	r_e(Ref. 3)	1.975	1.953	–	-0.021	–
SrF	calc.	2.096	2.079	2.096	-0.017	0.000
	r_e(Ref. 1)	2.075	–	2.080	–	0.005
SrOH	calc.	2.120	2.097	2.102	-0.024	-0.018
	r_0(Ref. 4)	2.111	2.091	2.098	-0.020	-0.013
BaF	calc.	2.195	2.209	2.237	0.014	0.042
	r_e(Ref. 1)	2.163	2.183	2.208	0.020	0.045
BaOH	calc.	2.223	2.226	2.245	0.003	0.022
	r_0(Ref. 5)	2.200	2.237	2.231	0.037	0.031

TABLE S3: Comparison of the calculated electron affinities (EA, eV) with the experimental values for selected species with the largest EAs. The calculated EAs were taken as the difference between the total electronic energies at the equilibrium geometries of the neutral and anionic states calculated using EOM-IP-CCSD (with anionic reference) and CCSD, respectively.

Molecule	Calc.	Exp.	Source
F	3.318	3.401	Ref. 6
NCO	3.652	3.609	Ref. 7
NC	3.989	3.862	Ref. 7
OBO	4.465	4.46	Ref. 8

TABLE S4: Compilation of Mulliken's and natural charge of the metal (Z), excitation energy (E_{ex}, eV), oscillator strength (f_{osc}), transition dipole moment (μ^{IF}, au) of the three lowest-energy electronic transitions calculated using EOM-EA-CCSD.

Molecule		Mulliken's Z	Natural Z	$X^2\Sigma^+ \rightarrow A^2\Pi$			$X^2\Sigma^+ \rightarrow B^2\Sigma^+$			$X^2\Sigma^+ \rightarrow A'^2\Delta$		
M	R			E_{ex}	f_{osc}	μ^{IF}	E_{ex}	f_{osc}	μ^{IF}	E_{ex}	f_{osc}	μ^{IF}
Ca	H	1.155	1.660	1.831	0.197	2.096	2.119	0.114	1.484	2.616	0.000	0.000
	CCH	1.262	1.862	1.995	0.224	2.141	2.221	0.156	1.692	2.704	0.000	0.000
	OH	1.395	1.871	2.034	0.261	2.287	2.341	0.197	1.854	2.981	0.000	0.000
	F	1.482	1.860	2.100	0.265	2.268	2.437	0.196	1.811	2.940	0.000	0.000
	NCO	1.539	1.899	2.088	0.235	2.144	2.282	0.173	1.760	2.756	0.000	0.000
	NC	1.545	1.899	2.104	0.223	2.082	2.281	0.158	1.680	2.675	0.000	0.000
	OBO	1.615	1.919	2.154	0.240	2.134	2.350	0.180	1.770	2.760	0.000	0.000
Sr	H	1.198	1.698	1.694	0.224	2.322	1.846	0.120	1.632	2.200	0.000	0.000
	CCH	1.460	1.887	1.813	0.233	2.292	1.960	0.164	1.846	2.292	0.000	0.000
	OH	1.424	1.895	1.835	0.275	2.473	2.069	0.205	2.011	2.497	0.000	0.000
	F	1.510	1.882	1.905	0.277	2.437	2.179	0.205	1.959	2.474	0.000	0.000
	NCO	1.560	1.926	1.901	0.244	2.290	2.040	0.182	1.910	2.345	0.000	0.000
	NC	1.583	1.922	1.913	0.228	2.206	2.048	0.168	1.831	2.296	0.000	0.000
	OBO	1.637	1.944	1.973	0.251	2.277	2.125	0.190	1.910	2.357	0.000	0.000
Ba	H	1.236	1.756	1.289	0.115	1.905	1.416	0.100	1.701	1.272	0.000	0.000
	CCH	1.550	1.900	1.300	0.109	1.849	1.486	0.131	1.897	1.302	0.000	0.000
	OH	1.430	1.891	1.471	0.240	2.580	1.642	0.179	2.109	1.519	0.000	0.000
	F	1.508	1.878	1.511	0.221	2.443	1.765	0.182	2.050	1.462	0.000	0.000
	NCO	1.589	1.926	1.402	0.135	1.979	1.562	0.145	1.948	1.324	0.000	0.000
	NC	1.615	1.929	1.334	0.099	1.738	1.540	0.130	1.855	1.260	0.000	0.000
	OBO	1.649	1.944	1.481	0.146	2.009	1.654	0.149	1.917	1.315	0.000	0.000

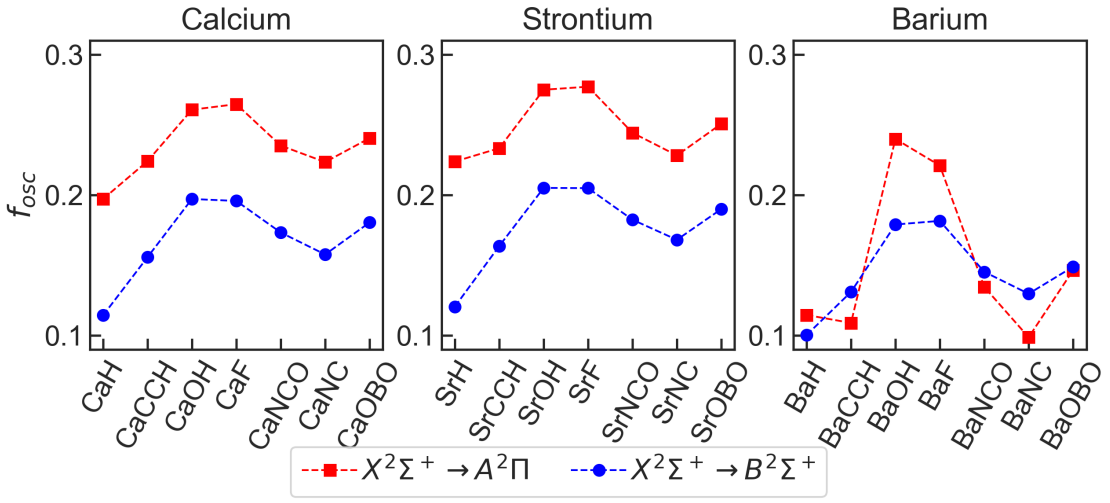

FIG. S2: Oscillator strengths of two bright lowest-energy transitions (as indicated) computed using EOM-EA-CCSD.

TABLE S5: Equilibrium bond lengths between the metal M and the directly connected atom of the ligand (R) in the three lowest energy electronic states and corresponding bond length changes (ΔR) between the lowest two excited states and the ground state calculated using EOM-EA-CCSD.

Molecule		R, Å			ΔR, Å	
M	R	$X^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$	$X^2\Sigma^+ - A^2\Pi$	$X^2\Sigma^+ - B^2\Sigma^+$
Ca	H	2.014	1.977	1.969	-0.034	-0.045
	CCH	2.331	2.296	2.294	-0.035	-0.036
	OH	1.988	1.962	1.964	-0.026	-0.024
	F	1.966	1.947	1.961	-0.019	-0.005
	NCO	2.157	2.128	2.131	-0.029	-0.026
	NC	2.207	2.182	2.187	-0.025	-0.020
	OBO	2.062	2.041	2.049	-0.020	-0.013
Sr	H	2.163	2.130	2.125	-0.034	-0.038
	CCH	2.480	2.446	2.448	-0.034	-0.032
	OH	2.120	2.097	2.102	-0.024	-0.018
	F	2.096	2.079	2.096	-0.017	-0.000
	NCO	2.301	2.275	2.279	-0.026	-0.022
	NC	2.354	2.331	2.338	-0.023	-0.016
	OBO	2.203	2.186	2.197	-0.016	-0.006
Ba	H	2.260	2.309	2.310	0.049	0.049
	CCH	2.600	2.616	2.639	0.016	0.039
	OH	2.223	2.226	2.245	0.003	0.022
	F	2.195	2.209	2.237	0.014	0.042
	NCO	2.423	2.454	2.465	0.031	0.042
	NC	2.482	2.538	2.538	0.056	0.057
	OBO	2.323	2.384	2.384	0.061	0.061

TABLE S6: FCFs for the decay transitions from the $A^2\Pi$ and $B^2\Sigma^+$ states to $X^2\Sigma^+$ in MOH molecules calculated with EOM-EA-CCSD within double-harmonic parallel-mode approximation using normal mode and frequencies of the ground state.

Transition	CaOH		SrOH		BaOH	
	$A^2\Pi$	$B^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma$
0_0^0	0.9168	0.9285	0.9153	0.9477	0.8716	0.9224
1_1^0	0.0796	0.0635	0.0810	0.0508	0.1197	0.0485
1_2^0	0.0035	0.0067	0.0036	0.0014	0.0082	0.0175

2. QUANTUM DEFECT THEORY FITS TO EOM-CC DATA

2.1. Quantum defects in Ca^+, Sr^+, Ba^+

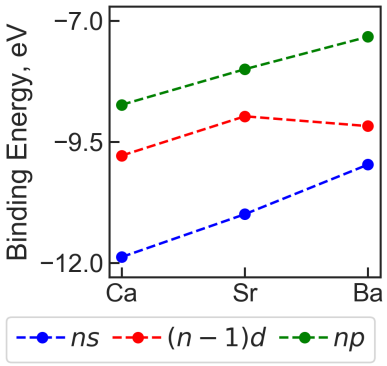

FIG. S3: Binding energies of Ca^+, Sr^+, and Ba^+.

TABLE S7: Binding energies E_{nl} of Ca^+, Sr^+ and Ba^+ in their valence states computed using EOM-EA-CCSD, and the corresponding quantum defects δ_l.

State	Ca^+	Sr^+	Ba^+
	E_{nl}		
ns	-11.88	-11.00	-9.97
$(n-1)d$	-9.79	-8.97	-9.18
np	-8.74	-8.00	-7.33
	δ_l		
ns	1.86	2.78	3.66
$(n-1)d$	0.64	1.54	2.56
np	1.50	2.39	3.27

2.2. Quantum defects in MR molecules

TABLE S8: Coefficients obtained by fitting the natural charges to the EOM-CC binding energies using second-order polynomial.

	$X^2\Sigma$	$A^2\Pi$	$B^2\Sigma$	$A'^2\Delta$
	CaR			
a	-41.7	-37.4	-43.3	-52.2
b	-3.5	-3.5	-3.5	-3.5
c	3.2	3.2	3.2	3.2
δ_l	3.4	3.4	3.4	2.5
	SrR			
a	-41.2	-35.7	-41.1	-48.9
b	-3.6	-3.6	-3.6	-3.6
c	3.3	3.3	3.3	3.3
δ_l	4.4	4.4	4.4	3.5
	BaR			
a	-57.9	-62.8	-77.4	-68.4
b	-3.6	-3.7	-3.7	-3.7
c	3.4	3.4	3.4	3.4
δ_l	5.5	5.5	5.6	4.6

TABLE S9: Coefficients obtained by fitting Mulliken's charges to the EOM-CC binding energies using second-order polynomial.

	$X^2\Sigma$	$A^2\Pi$	$B^2\Sigma$	$A'^2\Delta$
	CaR			
a	-6.0	-7.1	-8.0	-10.1
b	-2.5	-2.7	-2.6	-2.7
c	2.6	2.3	2.2	2.1
δ_l	2.5	2.6	2.7	1.8
	SrR			
a	-7.4	-7.0	-8.0	-9.7
b	-2.6	-2.7	-2.7	-2.7
c	2.4	2.3	2.2	2.1
δ_l	3.6	3.6	3.6	2.8
	BaR			
a	-10.4	-11.9	-14.9	-12.9
b	-2.7	-2.8	-2.8	-2.8
c	2.3	2.2	2.1	2.2
δ_l	4.9	4.9	5.0	4.0

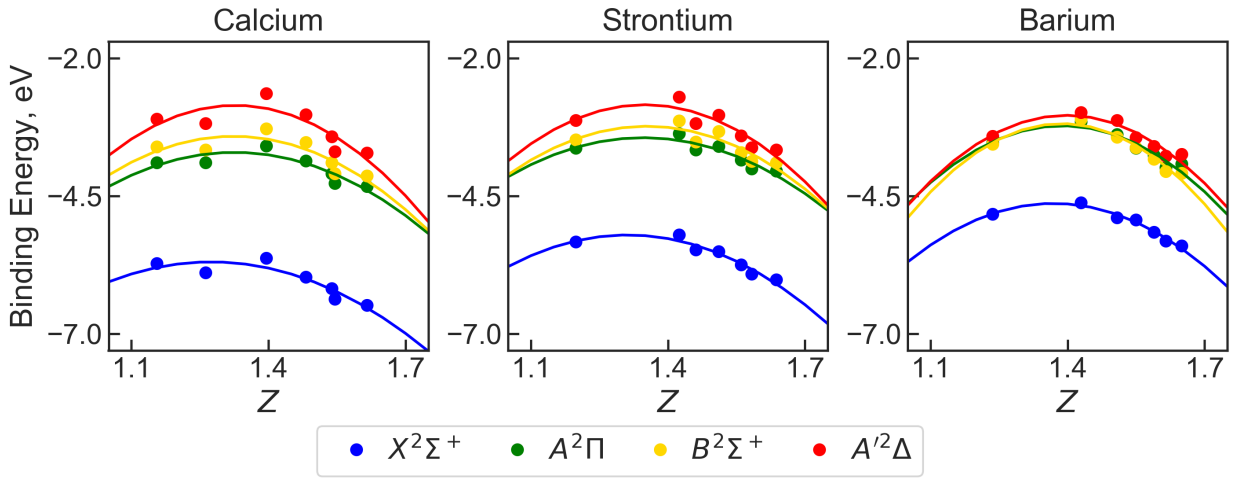

FIG. S4: Electron binding energies obtained with EOM-EA-CCSD versus Mulliken's charge of the metal.

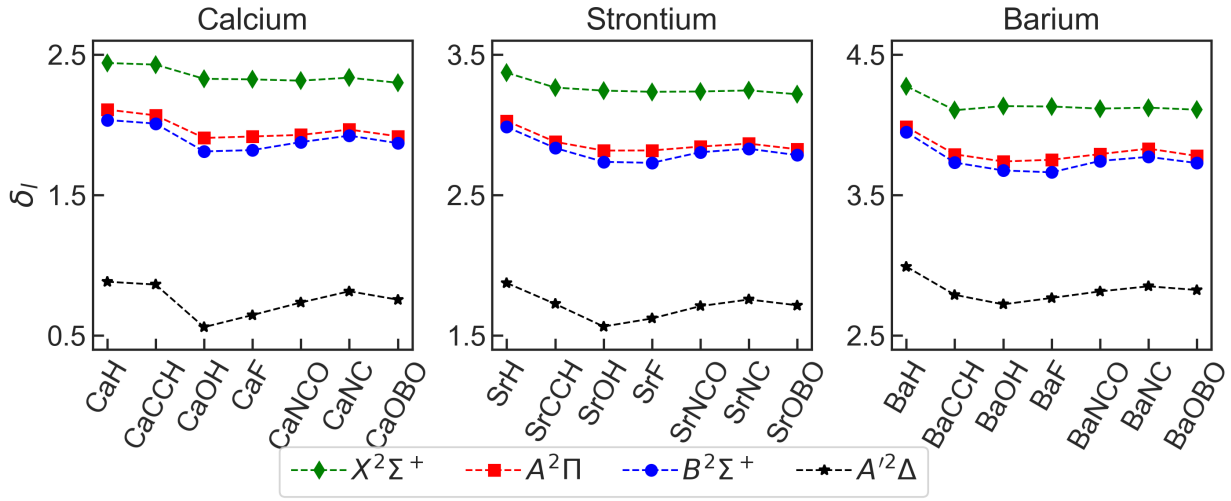

FIG. S5: Quantum defects δ_l versus Mulliken's charge of the metal.

TABLE S10: Quantum defects obtained using the natural charges.

M	State	H	CCH	OH	F	NCO	NC	OBO
Ca	X	2.15	1.99	1.94	2.01	2.00	2.04	2.03
	A	1.76	1.53	1.42	1.53	1.55	1.60	1.59
	B	1.67	1.46	1.30	1.41	1.49	1.55	1.54
	A′	0.49	0.27	-0.01	0.20	0.32	0.42	0.40
Sr	X	3.05	2.89	2.83	2.90	2.90	2.94	2.93
	A	2.64	2.42	2.30	2.41	2.44	2.49	2.48
	B	2.59	2.37	2.20	2.30	2.39	2.45	2.43
	A′	1.46	1.24	0.99	1.17	1.28	1.36	1.35
Ba	X	3.90	3.76	3.70	3.78	3.79	3.82	3.82
	A	3.54	3.39	3.22	3.33	3.41	3.48	3.44
	B	3.50	3.33	3.14	3.23	3.35	3.41	3.38
	A′	2.55	2.39	2.20	2.35	2.43	2.50	2.49

TABLE S11: Quantum defects obtained using Mulliken's charges.

M	State	H	CCH	OH	F	NCO	NC	OBO
Ca	X	2.44	2.43	2.33	2.32	2.31	2.34	2.30
	A	2.11	2.07	1.91	1.92	1.93	1.97	1.92
	B	2.03	2.01	1.81	1.82	1.88	1.92	1.87
	A′	0.88	0.86	0.56	0.65	0.73	0.81	0.75
Sr	X	3.37	3.26	3.24	3.23	3.24	3.24	3.22
	A	3.03	2.88	2.82	2.82	2.84	2.87	2.83
	B	2.98	2.83	2.74	2.73	2.80	2.83	2.78
	A′	1.87	1.72	1.56	1.62	1.71	1.76	1.71
Ba	X	4.28	4.10	4.13	4.13	4.12	4.12	4.11
	A	3.99	3.79	3.74	3.75	3.79	3.83	3.78
	B	3.95	3.73	3.67	3.66	3.74	3.77	3.73
	A′	2.99	2.79	2.72	2.77	2.81	2.85	2.82

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