Supporting Information

A Photoelectron Spectroscopic and Computational Study of Sodium Auride Clusters, Na_nAu_n^- ($n = 1-3$)

Li-Feng Cui,¹ Ying-Chan Lin, Dage Sundholm, and Lai-Sheng Wang

Table S1. Ground state electron configuration of NaAu^- : $^2\Sigma(6\sigma^23\pi^41\delta^47\sigma^28\sigma^1)$

Major Final State	Cal. VDE (C_s) (CC2/MP2)	Contribution	Expt. VDE
$^1\Sigma(6\sigma^23\pi^41\delta^47\sigma^28\sigma^0)$	0.714	100%	X, 0.77±0.025
$^3\Sigma(6\sigma^23\pi^41\delta^47\sigma^18\sigma^1)$	3.417 (T)	72%	A, 3.42±0.025
$^1\Sigma(6\sigma^23\pi^41\delta^47\sigma^18\sigma^1)$	3.906 (S)	76%	B, 3.89±0.025

Table S2. Ground state electron configuration of Na_2Au_2^- : $^2A'(8a''^220a'^221a'^222a'^223a'^1)$

Major Final State	Cal. VDE (C_s) (CC2/MP2)	Contribution	Expt. VDE
$^1A'(8a''^220a'^221a'^222a'^223a'^0)$	1.536	100%	X, 1.54±0.025
$^3A'(8a''^220a'^221a'^222a'^123a'^1)$	4.354 (T)	77%	A, 4.37±0.025
$^1A'(8a''^220a'^221a'^222a'^123a'^1)$	4.401 (S)	88%	

Table S3. Ground state electron configuration of Na_3Au_3^- : $^2A'(18a''^225a'^219a''^226a'^227a'^1)$

Major Final State	Cal. VDE (C_s) (CC2/MP2)	Contribution	Expt. VDE
$^1A'(18a''^225a'^219a''^226a'^227a'^0)$	1.138	100%	X, 1.20±0.025
$^3A'(18a''^225a'^219a''^226a'^127a'^1)$	4.023 (T)	69%	A, 4.03±0.025
$^3A''(18a''^225a'^219a''^126a'^227a'^1)$	4.242 (T)	60%	B, 4.25±0.025
$^1A'(18a''^225a'^219a''^226a'^127a'^1)$	4.342 (S)	80%	
$^1A''(18a''^225a'^219a''^126a'^227a'^1)$	4.547 (S)	77%	C, 4.61±0.040

I. NaAu & NaAu^-

NaAu structure of $C_{\infty v}$ symmetry

The coordinate of the NaAu structure of $C_{\infty v}$ symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	0.0000000000000000	0.0000000000000000	-0.50858004281252
Na	0.0000000000000000	0.0000000000000000	4.35736766012675

The NaAu and NaAu^- energies were obtained at different levels by using the NaAu structure optimized at RI-MP2 level.

Energies are given in atomic unit. (The zero point vibrational energy is 0.0005834 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
NaAu	-297.3983824841	-297.396915140995	-297.356777828774
NaAu^-	-297.4203753700	-297.418841107888	-297.376717536582

NaAu⁻ structure of C_{∞v} symmetry

The coordinate of the NaAu⁻ structure of C_{∞v} symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	0.0000000000000000	0.0000000000000000	-0.54374208666472
Na	0.0000000000000000	0.0000000000000000	4.65862594760935

The NaAu and NaAu⁻ energies were obtained at different levels by using the NaAu⁻ structure optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0004201 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
NaAu	297.3960035914	297.394532061055	297.355632063161
NaAu ⁻	297.4222514565	297.420703607166	297.379579636380

II. Na₂Au₂ & Na₂Au₂⁻

Na₂Au₂ structure of D_{2h} symmetry

The coordinate of the Na₂Au₂ structure of D_{2h} symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	0.0000000000000000	4.20518746144422	0.0000000000000000
Au	0.0000000000000000	-4.20518746144422	0.0000000000000000
Na	-3.11569682040370	0.0000000000000000	0.0000000000000000
Na	3.11569682040370	0.0000000000000000	0.0000000000000000

The Na₂Au₂ and Na₂Au₂⁻ energies were obtained at different levels by using the Na₂Au₂ structure of D_{2h} symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0019837 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na ₂ Au ₂	-594.8699586167	-	-
Na ₂ Au ₂ ⁻	-594.8799416265	-594.866978691928	-594.774377942521

Na₂Au₂⁻ structure of C_s symmetry --- quasi-linear

The coordinate of the Na₂Au₂⁻ structure of C_s symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	-0.61530255475458	-4.74812945098896	0.0000000000000000
Au	0.10864277044883	5.53285823349453	0.0000000000000000
Na	0.12378671469120	0.44653653015085	0.0000000000000000
Na	4.21712872235925	-7.16986723725243	0.0000000000000000

The Na₂Au₂ and Na₂Au₂⁻ energies were obtained at different levels by using the Na₂Au₂⁻ structure of C_s symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.00134 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na ₂ Au ₂	-594.8239070162	-594.820951726787	-594.736597587615
Na ₂ Au ₂ ⁻	-594.8803560004	-594.877354115617	-594.790151850670

Na₂Au₂⁻ structure of D_{2h} symmetry

The coordinate of the Na₂Au₂⁻ structure of D_{2h} symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	0.00000000000000	4.15756442302129	0.00000000000000
Au	0.00000000000000	-4.15756442302129	0.00000000000000
Na	-3.26868377262366	0.00000000000000	0.00000000000000
Na	3.26868377262366	0.00000000000000	0.00000000000000

The Na_2Au_2 and Na_2Au_2^- energies were obtained at different levels by using the Na_2Au_2^- structure of D_{2h} symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0022575 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_2Au_2	-594.8694525672	-594.866468141507	-594.773972380589
Na_2Au_2^-	-594.8804022729	-594.877374371834	-594.785120243730

III. Na_3Au_3

Na_3Au_3 structure of D_{3h} symmetry

The coordinate of the Na_3Au_3 structure of D_{3h} symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	2.86149764911977	-4.95625931401434	0.00000000000000
Au	2.86149764911977	4.95625931401434	0.00000000000000
Au	-5.72299529823954	0.00000000000000	0.00000000000000
Na	4.42817723715850	0.00000000000000	0.00000000000000
Na	-2.21408861857925	3.83491397983925	0.00000000000000
Na	-2.21408861857925	-3.83491397983925	0.00000000000000

The Na_3Au_3 and Na_3Au_3^- energies were obtained at different levels by using the Na_3Au_3 structure of D_{3h} symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0029770 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_3Au_3	-892.3246213356	-892.320162401951	-892.181538715882
Na_3Au_3^-	-892.3249896072	-	-

Na_3Au_3 structure of C_s symmetry --- bent flake

The coordinate of the Na_3Au_3 structure of C_s symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	-0.01495483818666	-2.39502646328219	5.10997448087139
Au	-0.01495483818666	-2.39502646328219	-5.10997448087139
Au	0.20456643521703	4.37090702205570	0.00000000000000
Na	-1.30835535502211	2.53177472824823	4.73353255217753
Na	1.12030179002547	-1.47242779336435	0.00000000000000
Na	-1.30835535502211	2.53177472824823	-4.73353255217753

The Na_3Au_3 and Na_3Au_3^- energies were obtained at different levels by using the Na_3Au_3 structure of C_s symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0030952 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_3Au_3	-892.3243493131	-892.319874173897	-892.178265962935
Na_3Au_3^-	-892.3366291475	-	-

Na_3Au_3 structure of C_s symmetry --- compact

The coordinate of the Na_3Au_3 structure of C_s symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	-0.00000480495573	-2.24672285877454	3.72583422660396
Au	-0.00000480495573	-2.24672285877454	-3.72583422660396
Au	0.00000383810518	5.00883277219766	0.00000000000000
Na	2.93968922156249	0.71076369017602	0.00000000000000
Na	0.00006925942574	-5.83719220359538	0.00000000000000
Na	-2.93970902981074	0.71074033195917	0.00000000000000

The Na_3Au_3 and Na_3Au_3^- energies were obtained at different levels by using the Na_3Au_3 structure of C_s symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0033649 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_3Au_3	-892.3275383408	-892.323054007031	-892.176399525719
Na_3Au_3^-	-	-	-

IV. Na_3Au_3^-

Na_3Au_3^- structure of C_s symmetry --- bent flake

The coordinate of the Na_3Au_3^- structure of C_s symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	0.41683199255511	-4.14754056691973	0.00000000000000
Au	0.05059691779788	2.21066565183673	-4.91192299326892
Au	0.05059691779788	2.21066565183673	4.91192299326892
Na	-3.13173916205706	-1.73261695506699	-3.29637279444782
Na	1.82518188957031	1.11947355474235	0.00000000000000
Na	-3.13173916205706	-1.73261695506699	3.29637279444782

The Na_3Au_3 and Na_3Au_3^- energies were obtained at different levels by using the Na_3Au_3^- structure of C_s symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0030649 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_3Au_3	-892.3080897194	-892.303619655719	-892.162855443678
Na_3Au_3^-	-892.3499232495	-892.345379319755	-892.201942541418

Na_3Au_3^- structure of C_s symmetry --- compact

The coordinate of the Na_3Au_3^- structure of C_s symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	-0.16873745292220	-2.31723891535716	3.57152703150477
Au	-0.16873745292220	-2.31723891535716	-3.57152703150477
Au	0.10804006481057	5.16795217927297	0.00000000000000
Na	2.88708852070385	0.60580881483270	0.00000000000000
Na	1.92248166701000	-5.86486714595230	0.00000000000000
Na	-2.84383840064159	0.68840341304305	0.00000000000000

The Na_3Au_3 and Na_3Au_3^- energies were obtained at different levels by using the Na_3Au_3^- structure of C_s symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0030719 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_3Au_3	-892.3182031835	-	-
Na_3Au_3^-	-892.3507274773	-892.346186131800	-892.199118969422

Na₃Au₃⁻ structure of C_s symmetry --- quasi-linear

The coordinate of the Na₃Au₃⁻ structure of C_s symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	-8.95270562143002	-0.89354974647084	0.000000000000000
Au	9.49854736708370	-1.72670829009474	0.000000000000000
Au	0.43862553243932	3.24980895923458	0.000000000000000
Na	-4.00123203757735	0.49281885407887	0.000000000000000
Na	4.95134845460349	0.45315070391852	0.000000000000000
Na	-9.38474915702292	-6.33978095427368	0.000000000000000

The Na₃Au₃ and Na₃Au₃⁻ energies were obtained at different levels by using the Na₃Au₃⁻ structure of C_s symmetry optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0022819 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na ₃ Au ₃	-892.2604742389	-	-
Na ₃ Au ₃ ⁻	-892.3289190519	-	-

V. Na₄Au₄ & Na₄Au₄⁻

Na₄Au₄ structure of T_d symmetry

The coordinate of the Na₄Au₄⁻ structure of T_d symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	2.93244066716965	2.93244066716965	-2.93244066716965
Au	-2.93244066716965	-2.93244066716965	-2.93244066716965
Au	-2.93244066716965	2.93244066716965	2.93244066716965
Au	2.93244066716965	-2.93244066716965	2.93244066716965
Na	2.41318473289126	-2.41318473289126	-2.41318473289126
Na	-2.41318473289126	2.41318473289126	-2.41318473289126
Na	-2.41318473289126	-2.41318473289126	2.41318473289126
Na	2.41318473289126	2.41318473289126	2.41318473289126

The Na₄Au₄ and Na₄Au₄⁻ energies were obtained at different levels by using the Na₄Au₄ structure optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0049196 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na ₄ Au ₄	-1189.8218495943	-	-
Na ₄ Au ₄ ⁻	-1189.8252015625	-	-

Na₄Au₄⁻ structure of C_{3v} symmetry

The coordinate of the Na₄Au₄⁻ structure of C₁ symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	0.00715914786614	5.32845015245181	0.000000000000000
Au	-4.73221706952445	-1.72666969931766	0.000000000000000
Au	2.36272786348310	-1.73688366410127	4.10242921015229
Au	2.36272786348310	-1.73688366410127	-4.10242921015229
Na	-1.88008860821794	1.31551672359373	-3.26036764182835
Na	-1.88008860821794	1.31551672359373	3.26036764182835
Na	-0.00666871979375	-5.02973494818494	0.000000000000000
Na	3.76343765466585	1.30192183271935	0.000000000000000

The Na_4Au_4 and Na_4Au_4^- energies were obtained at different levels by using the Na_4Au_4^- structure optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0045570 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_4Au_4	-1189.8159237596	-	-
Na_4Au_4^-	-1189.8284223008	-	-

Na_4Au_4^- structure of C_1 symmetry --- 01

The coordinate of the Na_4Au_4^- structure of C_1 symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	1.22212857477916	-2.50910484654647	1.55960388376395
Au	0.89580254327314	2.90507854474438	1.22059086581388
Au	3.78859330903977	0.29260611079931	-2.33537360776557
Au	-3.18570748008230	0.08376223548714	3.29489317140102
Na	-1.59831607035108	-0.24872915277216	-2.63119609283262
Na	5.41621427395833	0.84598315010046	3.08243721731409
Na	5.49549097635507	-4.44073174917432	-0.85326194848285
Na	-6.62173068562840	-0.24975609077623	-0.78246929479113

The Na_4Au_4 and Na_4Au_4^- energies were obtained at different levels by using the Na_4Au_4^- structure optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0047681 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_4Au_4	-1189.7802434080	-	-
Na_4Au_4^-	-1189.8286521404	-	-

Na_4Au_4^- structure of C_1 symmetry --- 02

The coordinate of the Na_4Au_4^- structure of C_1 symmetry optimized at RI-MP2 level.

	X	Y	Z
Au	-2.56089538775054	-1.93435238107883	1.50656912676563
Au	-0.05315886595675	1.76416004126722	-4.47095519664212
Au	2.32066048117784	-4.63842087139011	0.66979864256944
Au	0.77364265159183	5.60271955231250	2.46860525468119
Na	-2.48343492593997	-7.40172059847194	1.45481272717512
Na	-3.09953217183466	3.13296348031200	-0.15141475330813
Na	-0.87612170035929	-3.32911158922407	-3.42607941833285
Na	2.34445440771219	0.79419377290911	0.63174670567362

The Na_4Au_4 and Na_4Au_4^- energies were obtained at different levels by using the Na_4Au_4^- structure optimized at RI-MP2 level. Energies are given in atomic unit. (The zero point vibrational energy is 0.0044464 Hartree.)

Energy	RI-MP2	MBPT[2]	CCSD
Na_4Au_4	-1189.7723302484	-	-
Na_4Au_4^-	-1189.8252450049	-	-

VI. Energy gaps between HOMO, LUMO and between HOMO-1, HOMO. The Energies are given in eV.

(HF molecular orbitals)

Species	Symmetry	HOMO-1, HOMO	HOMO, LUMO
NaAu	$C_{\infty v}$	4.386	6.073
NaAu ⁻	$C_{\infty v}$	2.067	4.373
Na ₂ Au ₂	D_{2h}	1.333	6.309
Na ₂ Au ₂ ⁻	C_s	1.796	4.612
Na ₂ Au ₂ ⁻	D_{2h}	2.614	2.954
Na ₃ Au ₃	D_{3h}	0.933	7.243
Na ₃ Au ₃	C_s^a	0.051	6.269
Na ₃ Au ₃ ⁻	C_s	2.150	3.787
Na ₃ Au ₃ ⁻	C_s^a	2.178	3.368

a) The compact isomer of Cs symmetry.