SUPPORTING INFORMATION

Nb_2©Au_6: A Molecular Wheel with a Short Nb≡Nb Triple Bond Coordinated by an Au_6 Ring and Reinforced by σ Aromaticity

Tian Jian, Ling Fung Cheung, Joseph Czekner, Teng-Teng Chen, Gary V. Lopez, Wei-Li Li, and Lai-Sheng Wang*

Department of Chemistry, Brown University, Providence, Rhode Island 02912 (USA)

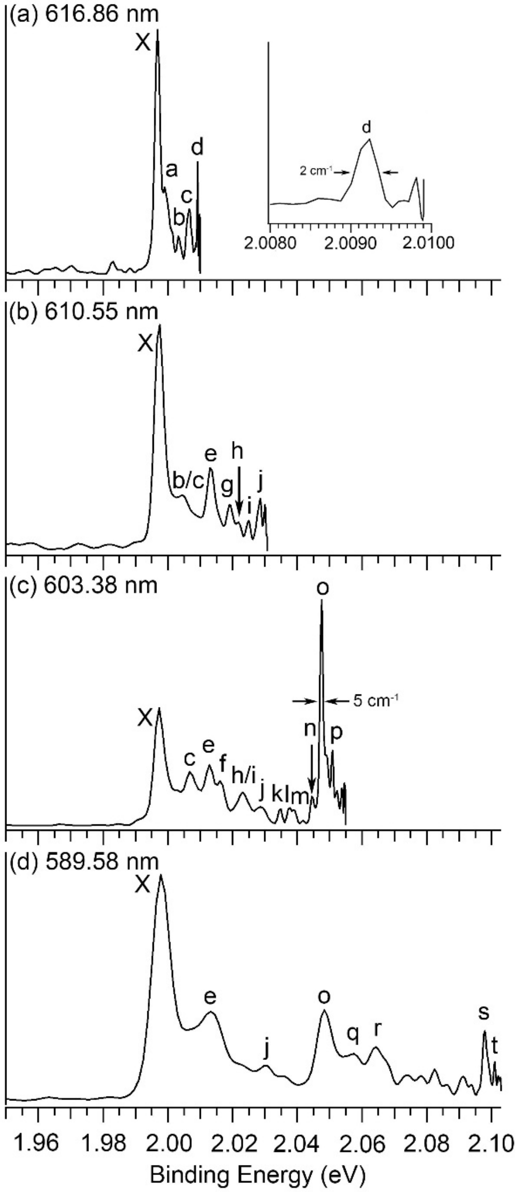
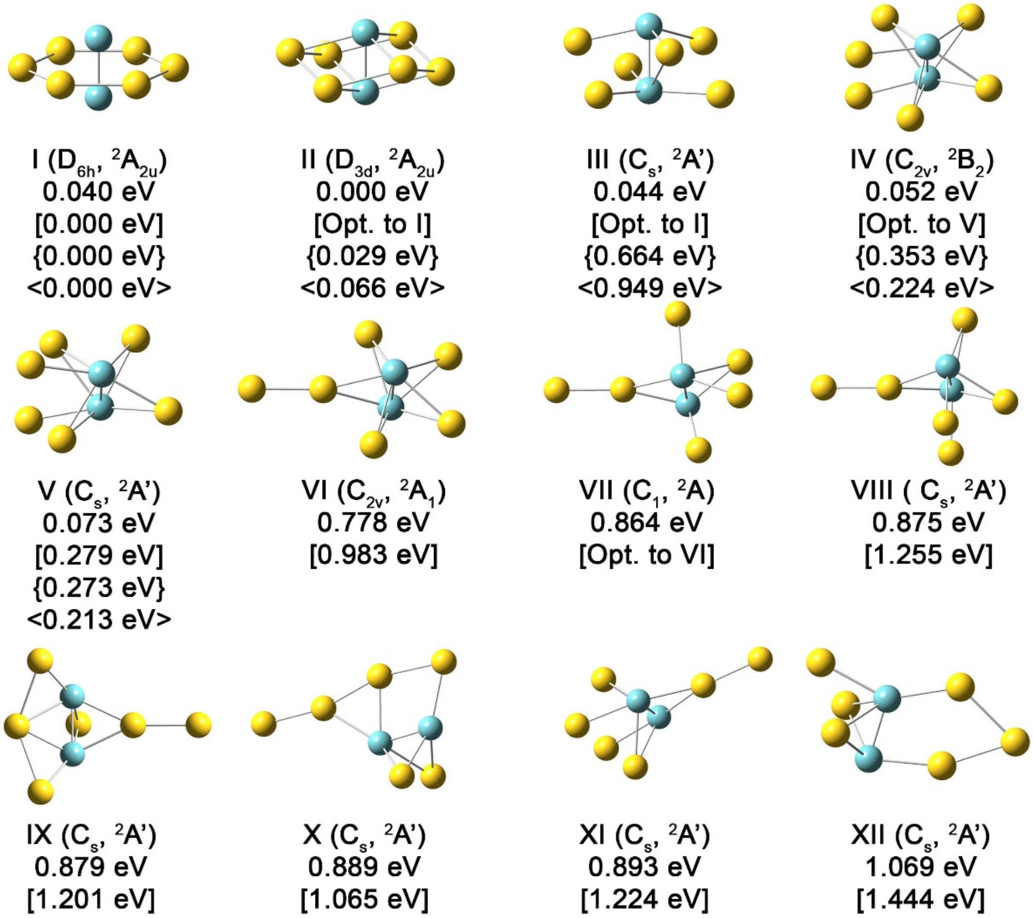


Figure S1. Photoelectron spectra of $Nb_2Au_6^-$ at a) 616.86 nm (2.0099 eV), b) 610.55 nm (2.0307 eV), c) 603.38 nm (2.0548 eV), and d) 589.58 nm (2.1029 eV) obtained from the VMI PES apparatus.


I (D_{6h}, $^2A_{2u}$)
0.040 eV
[0.000 eV]
{0.000 eV}
<0.000 eV>

II (D_{3d}, $^2A_{2u}$)
0.000 eV
[Opt. to I]
{0.029 eV}
<0.066 eV>

III (C_s, $^2A'$)
0.044 eV
[Opt. to I]
{0.664 eV}
<0.949 eV>

IV (C_{2v}, $^2B_2$)
0.052 eV
[Opt. to V]
{0.353 eV}
<0.224 eV>

V (C_s, $^2A'$)
0.073 eV
[0.279 eV]
{0.273 eV}
<0.213 eV>

VI (C_{2v}, $^2A_1$)
0.778 eV
[0.983 eV]

VII (C_1, ^2A)
0.864 eV
[Opt. to VI]

VIII (C_s, $^2A'$)
0.875 eV
[1.255 eV]

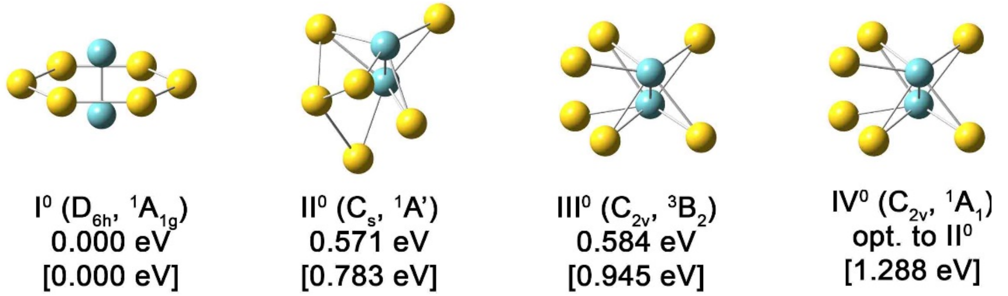
IX (C_s, $^2A'$)
0.879 eV
[1.201 eV]

X (C_s, $^2A'$)
0.889 eV
[1.065 eV]

XI (C_s, $^2A'$)
0.893 eV
[1.224 eV]

XII (C_s, $^2A'$)
1.069 eV
[1.444 eV]

Figure S2. Relative energies of the low-lying isomers of $Nb_2Au_6^-$ within 1.5 eV at the PW91, PBE0 (in square brackets), CCSD (in braces) and CCSD(T) (in angle brackets) levels.

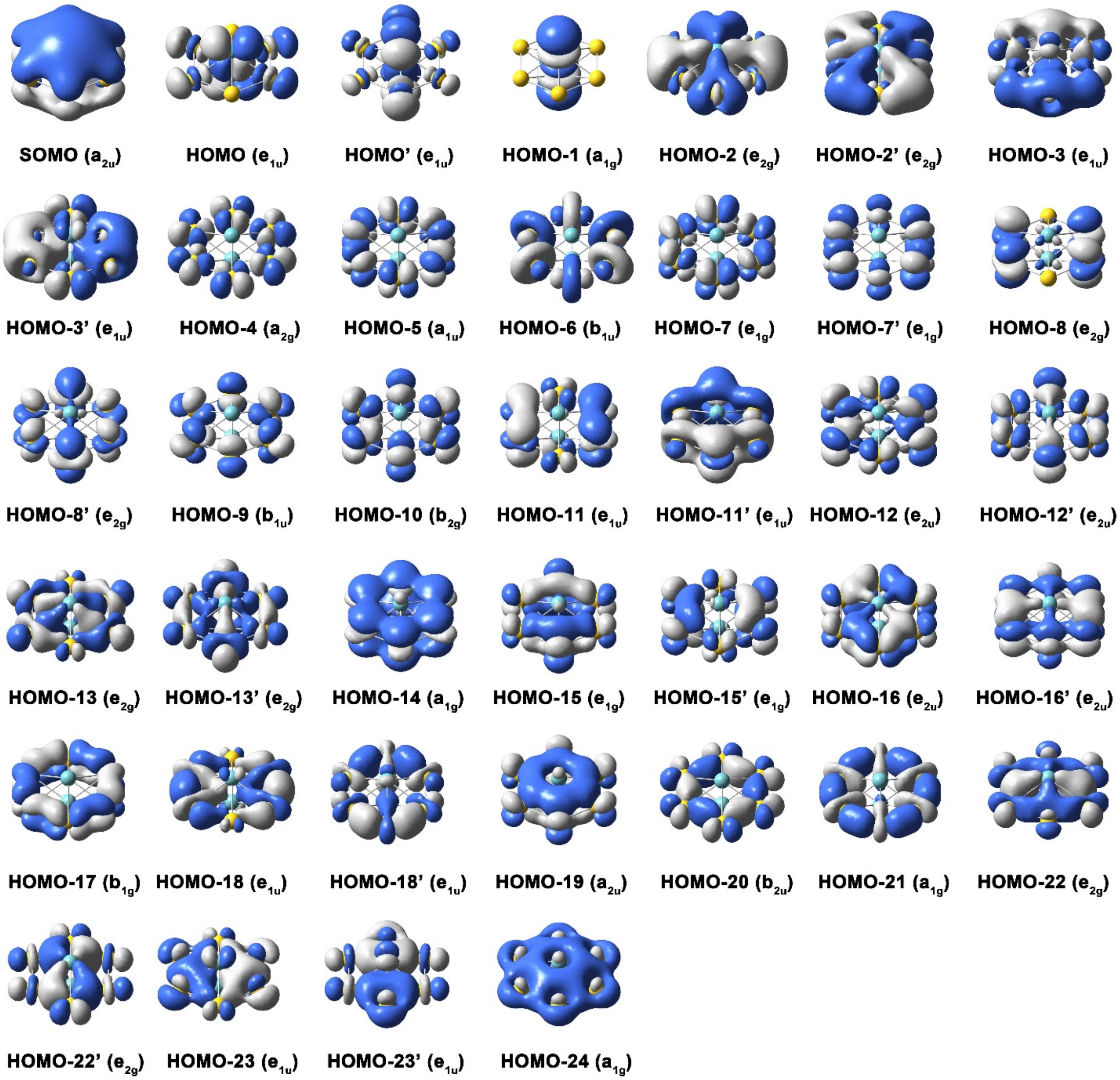

I^0 (D_{6h}, $^1A_{1g}$)
0.000 eV
[0.000 eV]

II^0 (C_s, $^1A'$)
0.571 eV
[0.783 eV]

III^0 (C_{2v}, $^3B_2$)
0.584 eV
[0.945 eV]

IV^0 (C_{2v}, $^1A_1$)
opt. to II^0
[1.288 eV]

Figure S3. The four lowest-lying isomers of Nb_2Au_6 at the levels of PW91 and PBE0 (in brackets).



SOMO (a_{2u}) **HOMO (e_{1u})** **HOMO' (e_{1u})** **HOMO-1 (a_{1g})** **HOMO-2 (e_{2g})** **HOMO-2' (e_{2g})** **HOMO-3 (e_{1u})**

HOMO-3' (e_{1u}) **HOMO-4 (a_{2g})** **HOMO-5 (a_{1u})** **HOMO-6 (b_{1u})** **HOMO-7 (e_{1g})** **HOMO-7' (e_{1g})** **HOMO-8 (e_{2g})**

HOMO-8' (e_{2g}) **HOMO-9 (b_{1u})** **HOMO-10 (b_{2g})** **HOMO-11 (e_{1u})** **HOMO-11' (e_{1u})** **HOMO-12 (e_{2u})** **HOMO-12' (e_{2u})**

HOMO-13 (e_{2g}) **HOMO-13' (e_{2g})** **HOMO-14 (a_{1g})** **HOMO-15 (e_{1g})** **HOMO-15' (e_{1g})** **HOMO-16 (e_{2u})** **HOMO-16' (e_{2u})**

HOMO-17 (b_{1g}) **HOMO-18 (e_{1u})** **HOMO-18' (e_{1u})** **HOMO-19 (a_{2u})** **HOMO-20 (b_{2u})** **HOMO-21 (a_{1g})** **HOMO-22 (e_{2g})**

HOMO-22' (e_{2g}) **HOMO-23 (e_{1u})** **HOMO-23' (e_{1u})** **HOMO-24 (a_{1g})**

Figure S4. Valence canonical molecular orbital contours for the D_{6h} $Nb_2Au_6^-$ structure at the PBE0 level.

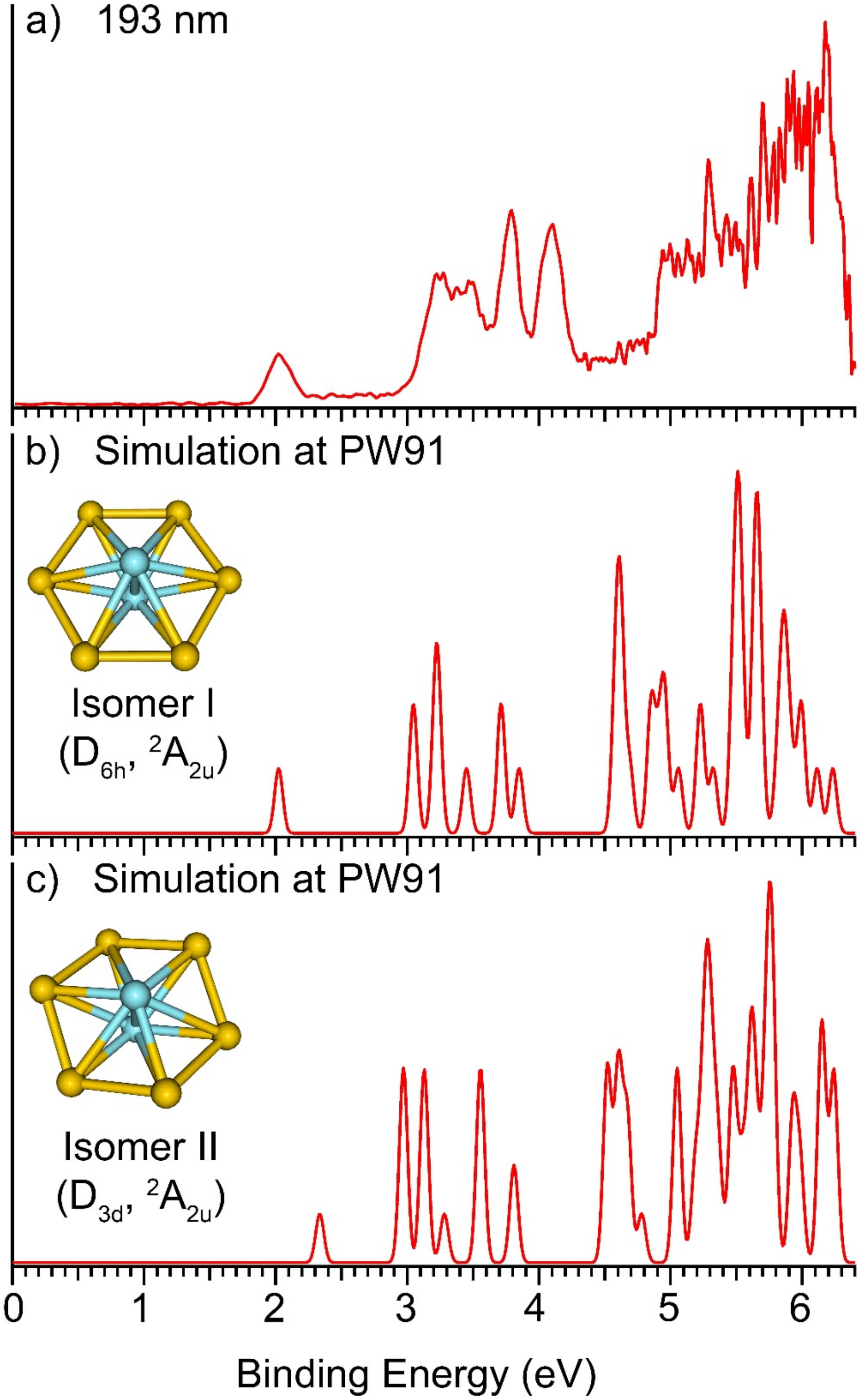


Figure S5. Comparison between the 193 nm spectrum of $Nb_2Au_6^-$ with the simulated spectra of isomers I and II at the PW91/Def2-TZVPPD level.

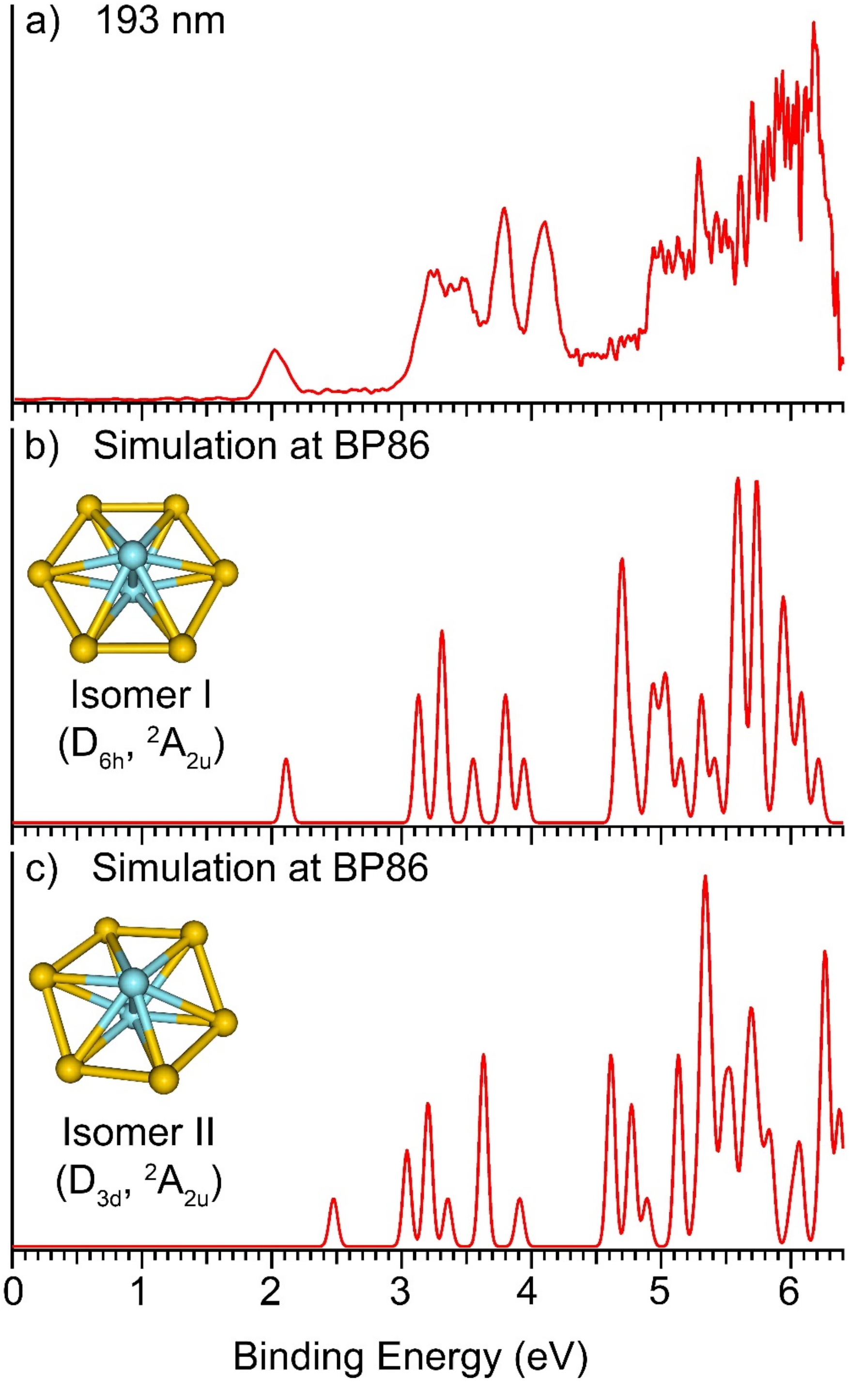


Figure S6. Comparison between the 193 nm spectrum of $Nb_2Au_6^-$ with the simulated spectra of isomers I and II at the BP86/Def2-TZVPPD level.

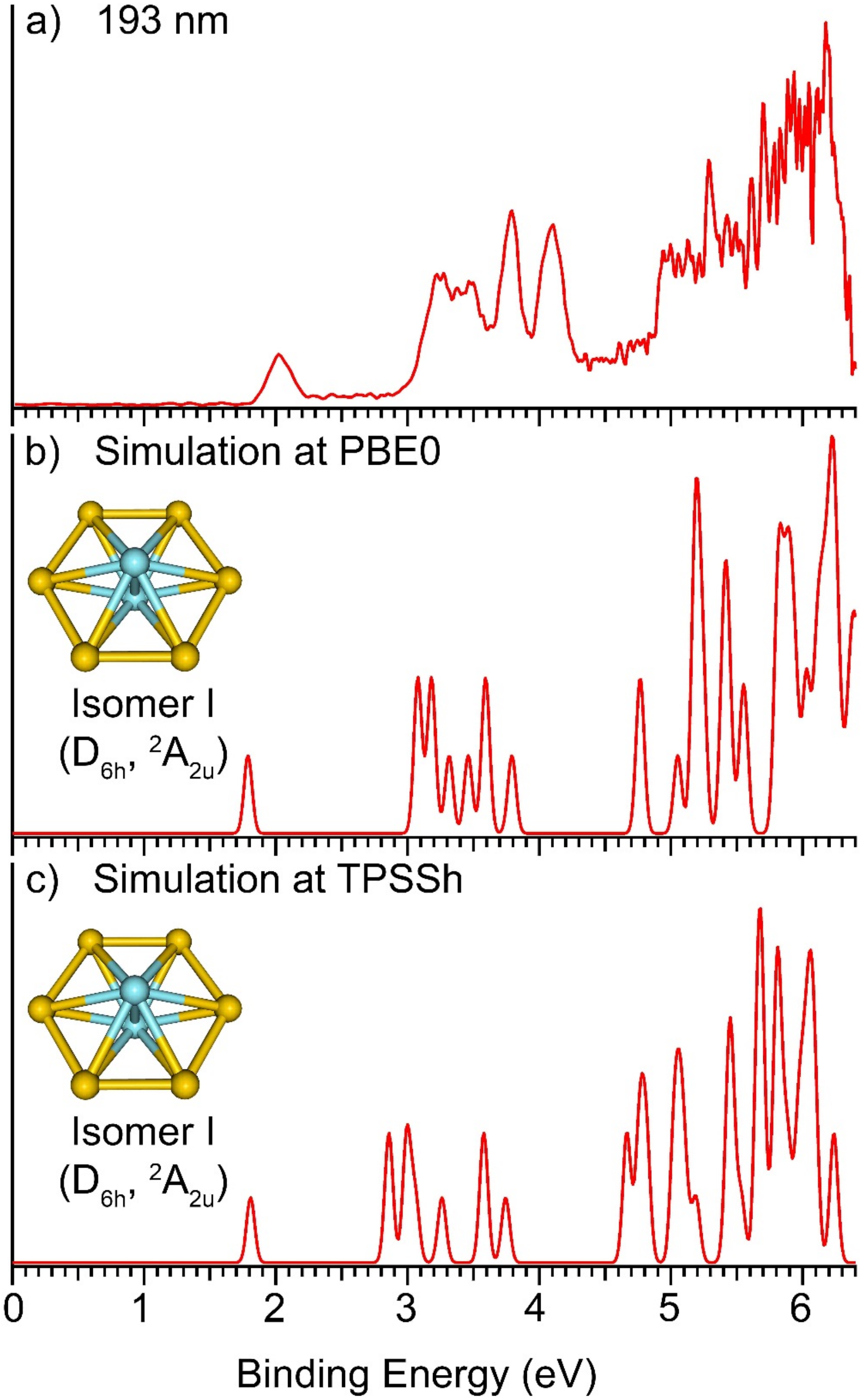


Figure S7. Comparison between the 193 nm spectrum of $Nb_2Au_6^-$ with the simulated spectra of isomer I at PBE0/Def2-TZVPPD and TPSSh/Def2-TZVPPD levels.

Table S1. The energy difference between isomers I and II of $Nb_2Au_6^-$ calculated at various levels of theory.

Method		Most Stable Isomer	ΔE(II-I) (eV)
GGA	PW91	II	-0.039
	PBE	II	-0.031
	BP86	II	-0.057
Hybrid-GGA	B3PB6	II	-0.015
Meta-GGA	TPSS	II	-0.004
Hybrid-GGA	PBE0	I	0.035[a]
Hybrid-Meta-GGA	TPSSh	I	0.031[a]
Long-range corrected	LC-ωPBE	I	0.133[a]
Post-HF	CCSD	I	0.029[a]
	CCSD(T)	I	0.066[a]

[a] Isomer II does not meet the convergence criteria of geometric optimization at these levels, the energy difference is obtained by single-point energy calculations using PW91/Def2-TZVPPD structures.

Table S2. The first VDEs of isomers I, II, III, IV and V of $Nb_2Au_6^-$ computed at the PW91 and PBE0 levels. All energies are in eV. Experimental first ADE and VDE: 1.9969(4) eV

	PW91		PBE0	
Isomer	1st VDE	1st ADE	1st VDE	1st ADE
I	2.02	2.01	1.79	1.77
II	2.33	2.05	N.A.	N.A.
III	2.99	2.00	N.A.	N.A.
IV	3.00	2.57	N.A.	N.A.
V	2.81	2.54	2.53	2.28

Table S3. Calculated vibrational frequencies for the D_{6h} global minimum of Nb_2Au_6 at PW91 and PBE0 levels. The totally symmetric vibrational modes are in boldface.

		PW91	PBE0
Mode	Symmetry	Frequency (cm^{-1})	Frequency (cm^{-1})
ν_1	E_{2u}	24	26
ν_2	B_{2g}	32	35
ν_3	E_{1g}	48	68
ν_4	E_{2g}	71	72
ν_5	B_{1u}	71	73
ν_6	A_{2u}	76	77
ν_7	E_{1u}	81	83
$\boldsymbol{\nu_8}$	$\mathbf{A_{1g}}$	**121**	**121**
ν_9	E_{2g}	131	130
ν_{10}	B_{2u}	143	142
ν_{11}	E_{1u}	163	166
$\boldsymbol{\nu_{12}}$	$\mathbf{A_{1g}}$	**423**	**460**

Table S4. Calculated bond orders and charges of $D_{\infty h}$ Nb_2, D_{6h} Au_6, and D_{6h} Nb_2Au_6 at the PBE0/Def2-TZVP level.

	Mayer Bond order			NPA Charge		Mulliken Charge	
	Nb-Nb	Nb-Au	Au-Au	Nb	Au	Nb	Au
Nb_2	5.07	NA	NA	0	NA	0	NA
Au_6	NA	NA	0.55	NA	0	NA	0
Nb_2Au_6	3.61	0.50	0.22	-0.195	0.065	-0.457	0.152