

Evidence of Significant Covalent Bonding in $\text{Au}(\text{CN})_2^-$

Xue-Bin Wang,¹ Yi-Lei Wang,² Jie Yang,¹ Xiao-Peng Xing,¹ Jun Li,^{2*} and Lai-Sheng Wang^{3*}

¹*Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99354, and Chemical & Materials Sciences Division, Pacific Northwest National Laboratory, MS K8-88, P. O. Box 999, Richland, Washington 99352*

²*Department of Chemistry & Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China*

³*Department of Chemistry, Brown University, Providence, RI 02912*

E-mails: junli@tsinghua.edu.cn; lai-sheng_wang@brown.edu

Experimental Methods

Low-temperature photoelectron spectroscopy (PES). The PES experiments were performed with a low-temperature apparatus equipped with an electrospray ion source (ESI) and a temperature-controlled ion trap^{S1} for the 193 nm (6.424 eV) and 157 nm (7.866 eV) data. The 118 nm data was obtained with a room temperature apparatus.^{S2} Solutions of 10^{-4} M $\text{KM}(\text{CN})_2$ ($\text{M} = \text{Cu}, \text{Ag}$ and Au) in a water/methanol mixed solvent (1/3 volume ratio) were used for the electrospray. For the low-temperature data, the $\text{M}(\text{CN})_2^-$ anions produced from the ESI source were guided by a radio-frequency only quadrupole and an octopole into a three-dimension Paul trap, where they were accumulated and cooled via collisions with a background gas of 0.1 mTorr helium for 100 ms before being pulsed out into the extraction zone of a TOF mass spectrometer for mass/charge analyses. In the current study, the lowest ion trap temperature of 12 K was used. Photoelectron time-of-flight spectra were collected and then converted to kinetic energy spectra, calibrated by the known spectra of I^- and ClO_2^- . The electron kinetic energy resolution ($\Delta\text{KE}/\text{KE}$) was $\sim 2\%$, i.e. 20 meV for 1 eV electrons. The electron binding energy spectra presented were obtained by subtracting the kinetic energy spectra from the detachment photon energies.

Photoelectron spectroscopy of $\text{Au}(\text{CN})_2^-$ at 118 nm. For the $\text{Au}(\text{CN})_2^-$ complex, PES data were also obtained using the ninth harmonics of a Nd:YAG laser (118.2 nm, 10.488 eV) to reach electron binding energies beyond 7.8 eV. The experiment was done using our room temperature apparatus, as described previously.^{S2} The 118 nm photons were generated using a four-wave mixing scheme by focusing the 355 nm light into a rare gas cell containing 1:10 Xe/Ar mixed gas. Special cares were taken to collimate the light through a series of pin-holes to minimize the noise due to the scattering light. A detailed account of the 118 nm light source and its coupling with the room-temperature ESI-PES spectrometer has been reported previously.^{S3}

Theoretical Calculations

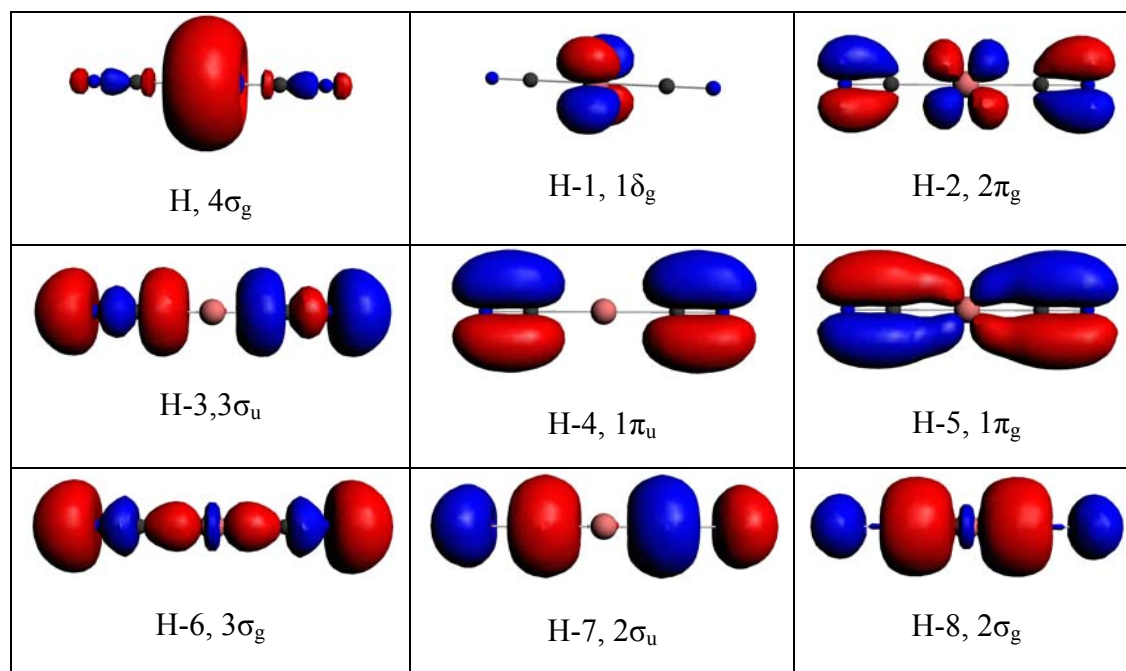
Geometries were optimized at the DFT PW91/TZ2P level with the frozen cores, Cu.3p, Ag.4p, Au.4f, C.1s, N.1s using ADF 2007.1. Vibrational frequency calculations were carried out to confirm that the species are true minima (Note: Cu(CN)₂ possesses a very soft bending mode that results in a small imaginary frequency of 15i cm⁻¹). Electron localization function (ELF) analysis was performed with the DGrid 4.1 program.^{S4} In the *ab initio* calculations, scalar-relativistic effective core potentials, ECP10MDF for Cu, ECP28MDF for Ag and ECP60MDF for Au, were employed. The aug-cc-pVTZ-PP basis sets (11s10p9d3f2g)/[6s6p5d3f2g] for Cu, Ag, and Au and aug-cc-pVTZ basis sets for C and O (denoted as AVTZ in this work) were used. In the CASSCF/CCSD(T)/SO approach, spin-orbit (SO)-free energies were obtained with UCCSD(T) while the SO matrix elements at the CASSCF level. For Au(CN)₂⁻, 21 electrons in 15 orbitals were used in the CASCF calculations, i.e., CASSCF(21e,15o). For Cu(CN)₂⁻ and Ag(CN)₂⁻, CASSCF(17e,13o) and CASSCF(23e,16o) were used, respectively. The active spaces were determined according to the low-lying excited states concerned. For Cu(CN)₂⁻, the high-lying states, ²Σ_u and ²Π_u, are only slightly affected by the SO effects and are not included in the SO calculations. Charge populations were analyzed using the NPA (natural population analysis),^{S5} Hershfeld,^{S6} Voronoi,^{S7} and MDC-q^{S8} methods. Bond orders were analyzed using the Wiberg,^{S9} G-J (Gopinathan-Jug),^{S10} and N-M (Nalewajski-Mrozek) (3)^{S11} methods.

References

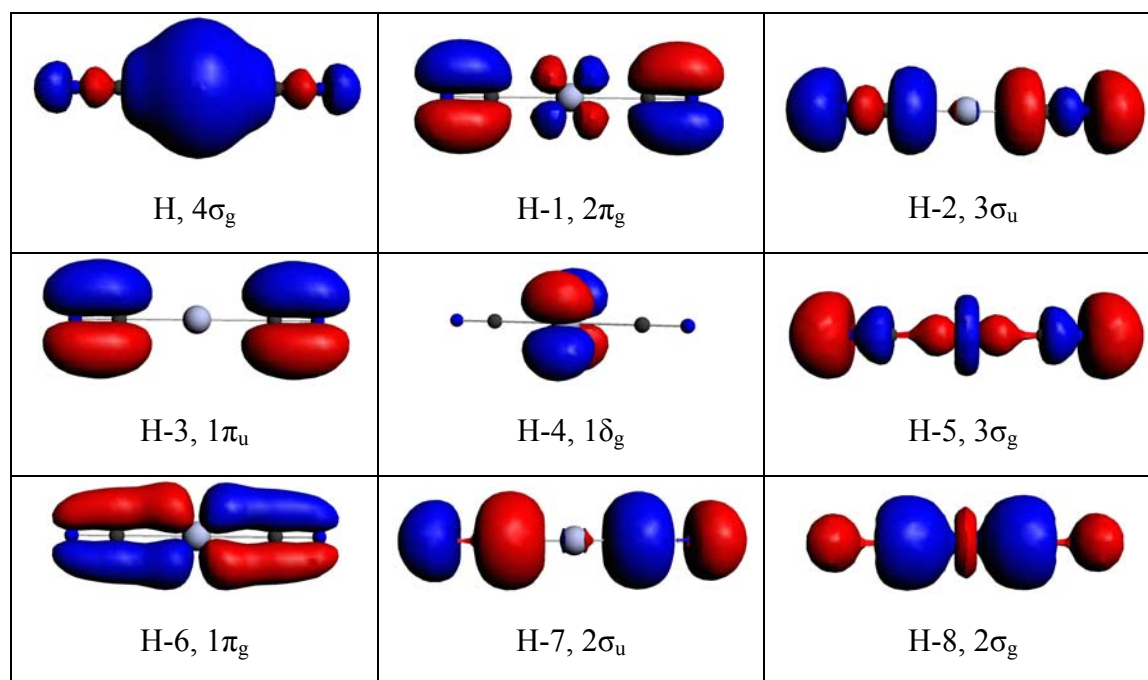
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Figure S1. Frontier occupied molecular orbitals of $M(\text{CN})_2^-$ ($M = \text{Cu}, \text{Ag}, \text{Au}$) with an isocontour value of 0.03 a.u.

(a) $\text{Cu}(\text{CN})_2^-$



(b) $\text{Ag}(\text{CN})_2^-$



(c) $\text{Au}(\text{CN})_2^-$ (Figure S1 continued)

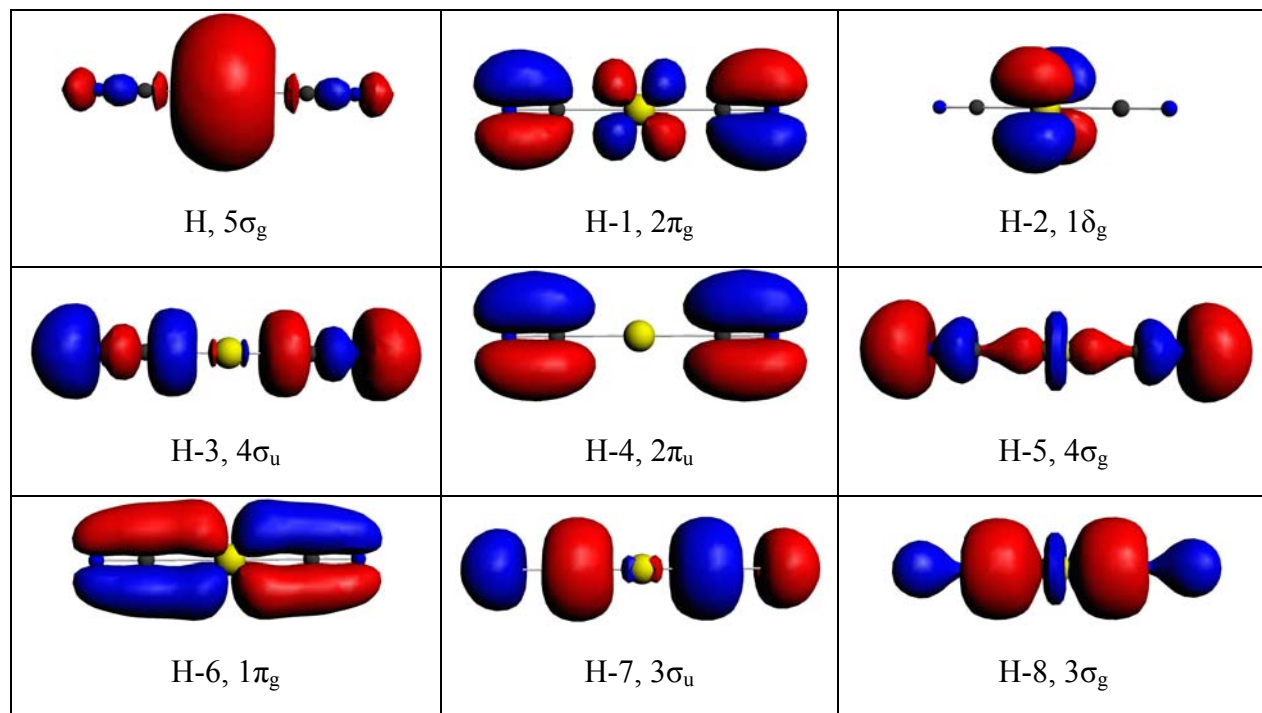


Table S1. Bond lengths ($\text{\AA}$) of $\text{M}(\text{CN})_2^q$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$, $q = 0, -1$) at the SR (scalar relativistic) and SO (spin-orbit) PW91 level of theory.

M	M-C		C-N	
	$q = -1$	$q = 0$	$q = -1$	$q = 0$
SR				
Cu	1.888	1.889	1.171	1.165
Ag	2.071	2.050	1.169	1.165
Au	1.994	1.993	1.170	1.164
SO				
Cu	1.888	1.881	1.171	1.172
Ag	2.071	2.049	1.169	1.166
Au	1.992	1.974	1.170	1.177

Table S2. Assignments of the Photoelectron Spectra for $M(CN)_2^-$ ($M = Cu, Ag, Au$) and Contribution of SO-free State to SO Eigenstates.

$Cu(CN)_2^-$			
Features	Expt.	Calc.	contribution of SO-free state to SO eigenstates
ADE	5.29	5.22	
VDE			
X	5.29	5.22	97% $[^2\Sigma_{1/2g}]$, 3% $[^2\Pi_{1/2g}]$
A	5.80	5.76	97% $[^2\Pi_{3/2g}]$, 3% $[^2\Delta_{3/2g}]$
B	5.92	5.88	97% $[^2\Pi_{1/2g}]$, 3% $[^2\Sigma_{1/2g}]$
C	~6.15	6.10	100% $[^2\Delta_{5/2g}]$
D	~6.4	6.29	97% $[^2\Delta_{3/2g}]$, 3% $[^2\Pi_{3/2g}]$
E	7.10	7.07	$^2\Sigma_u$
F	7.51	7.61	$^2\Pi_u$

$Ag(CN)_2^-$			
features	Expt.	Calc.	contribution of SO-free state to SO eigenstates
ADE	6.06	6.03	
VDE			
X	6.06	6.07	97% $[^2\Sigma_{1/2g}]$, 3% $[^2\Pi_{1/2g}]$
A	6.87	6.92	99% $[^2\Pi_{3/2g}]$, 1% $[^2\Delta_{3/2g}]$
B	6.96	7.04	100% $[^2\Sigma_{1/2u}]$
C	7.21	7.13	97% $[^2\Pi_{1/2g}]$, 3% $[^2\Sigma_{1/2g}]$
D	7.67	7.71	100% $[^2\Pi_{3/2u}]$
		7.71	100% $[^2\Pi_{1/2u}]$
		8.09	100% $[^2\Delta_{5/2g}]$
		8.51	99% $[^2\Delta_{3/2g}]$, 1% $[^2\Pi_{3/2g}]$

$Au(CN)_2^-$			
Feature	Expt.	Calc.	contribution of SO-free state to SO eigenstates
ADE	6.09	6.02	
VDE			
X	6.09	6.02	75% $[^2\Sigma_{1/2g}]$, 25% $[^2\Pi_{1/2g}]$
A	6.30	6.28	92% $[^2\Pi_{3/2g}]$, 8% $[^2\Delta_{3/2g}]$
B	6.83	6.94	100% $[^2\Delta_{5/2g}]$
C	7.31	7.24	75% $[^2\Pi_{1/2g}]$, 25% $[^2\Sigma_{1/2g}]$
		7.32	99% $[^2\Sigma_{1/2u}]$, 1% $[^2\Pi_{1/2u}]$
D	7.76	7.87	100% $[^2\Pi_{3/2u}]$
		7.88	99% $[^2\Pi_{1/2u}]$, 1% $[^2\Sigma_{1/2u}]$
E	8.50	8.35	92% $[^2\Delta_{3/2g}]$, 8% $[^2\Pi_{3/2g}]$

Table S3. Fragment analysis for $M(CN)_2^-$ ($M = Cu, Ag, Au$) with the M and CN neutrals as fragments (Unit: eV).^a

compounds	$Cu(CN)_2^-$		$Ag(CN)_2^-$		$Au(CN)_2^-$	
	SR	Δ_{SR-NR}	SR	Δ_{SR-NR}	SR	Δ_{SR-NR}
Pauli repulsion	14.25	-0.02	12.60	-0.10	20.31	-0.09
electrostatic interaction	-6.09	0.03	-5.51	0.08	-8.80	-0.01
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total steric interaction	8.16	0.01	7.10	-0.03	11.51	-0.10
σ_g	-13.51	-0.11	-11.76	-0.18	-16.07	-1.14
σ_u	-6.92	0.02	-6.76	0.03	-7.63	-0.09
π_g	-0.78	-0.01	-0.51	-0.01	-1.04	-0.21
π_u	-0.15	0.00	-0.11	0.00	-0.21	0.04
δ_g	0.07	0.00	0.01	0.00	0.02	0.01
	-----		-----		-----	
total orbital interactions	-21.29	-0.09	-19.14	-0.16	-24.94	-1.38
steric interaction	8.16	0.01	7.10	-0.03	11.51	-0.10
orbital interactions	-21.29	-0.09	-19.14	-0.16	-24.94	-1.38
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total bonding energies	-13.13	-0.08	-12.04	-0.19	-13.43	-1.48

^a The energy changes from non- to scalar relativistic effects are listed in the Δ_{SR-NR} columns. It is clear that the remarkable stabilization of $Au(CN)_2^-$ relative to that of the $Cu(CN)_2^-$ and $Ag(CN)_2^-$ complexes mainly results from the σ_g orbital interactions due to relativistic effects.

Table S4. Theoretical stretching vibrational frequencies (cm^{-1}) of $\text{M}(\text{CN})_2^-$ (M=Cu, Ag, Au)

compounds	M-C		C-N	
	sym.	asym.	sym.	asym.
$\text{Cu}(\text{CN})_2^-$	372	430	2145	2129
$\text{Ag}(\text{CN})_2^-$	333	366	2156	2148
$\text{Au}(\text{CN})_2^-$	433	412	2163	2145

Cartesian coordinates for linear $M(CN)_2^q$ ($M=Cu, Ag, Au, q = 0, -1$) at the PW91 level of theory.

$Cu(CN)_2$

1.Cu	0.000000	0.000000	0.000000
2.C	0.000000	0.000000	1.889351
3.N	0.000000	0.000000	3.054359
4.C	0.000000	0.000000	-1.889351
5.N	0.000000	0.000000	-3.054359

$Cu(CN)_2^-$

1.Cu	0.000000	0.000000	0.000000
2.C	0.000000	0.000000	1.887667
3.N	0.000000	0.000000	3.059152
4.C	0.000000	0.000000	-1.887667
5.N	0.000000	0.000000	-3.059152

$Ag(CN)_2$

1.Ag	0.000000	0.000000	0.000000
2.C	0.000000	0.000000	2.050365
3.N	0.000000	0.000000	3.215739
4.C	0.000000	0.000000	-2.050365
5.N	0.000000	0.000000	-3.215739

$Ag(CN)_2^-$

1.Ag	0.000000	0.000000	0.000000
2.C	0.000000	0.000000	2.070962
3.N	0.000000	0.000000	3.240233
4.C	0.000000	0.000000	-2.070962
5.N	0.000000	0.000000	-3.240233

$Au(CN)_2$

1.Au	0.000000	0.000000	0.000000
2.C	0.000000	0.000000	1.993126
3.N	0.000000	0.000000	3.157322
4.C	0.000000	0.000000	-1.993126
5.N	0.000000	0.000000	-3.157322

$Au(CN)_2^-$

1.Au	0.000000	0.000000	0.000000
2.C	0.000000	0.000000	1.994399
3.N	0.000000	0.000000	3.164065
4.C	0.000000	0.000000	-1.994399
5.N	0.000000	0.000000	-3.164065