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SUPPORTING INFORMATION

Spin-orbit and Relativistic All-electron Potential Energy Curves for the Ground and Low-lying Excited States of AgAu

Davood Alizadeh[a], *Zahra Jamshidi*[b,*] *and Alireza Shayesteh*[a,*]

[a] School of Chemistry, College of Science, University of Tehran, 14176, Tehran, Iran

[b] Chemistry and Chemical Engineering Research Center of Iran, 14335-186, Tehran, Iran

* Corresponding authors.

E-mails: jamshidi@ccerci.ac.ir , ashayesteh@ut.ac.ir

Table S1. The Ω states resulting from (Λ , S) states.

(Λ, S)coupling	**Ω = |Λ + Σ|**
$^1\Sigma^+$	0^+
$^1\Sigma^-$	0^-
$^3\Sigma^+$	$1, 0^-$
$^3\Sigma^-$	$1, 0^+$
$^1\Pi$	1
$^1\Delta$	2
$^3\Pi$	$2, 1, 0^+, 0^-$
$^3\Delta$	3, 2, 1

Table S2. Vibrational progression of AgAu calculated at the three levels of theory for three states for which experimental data is available. MAD stands for Mean Absolute deviation from the observed frequencies (all values are in cm^{-1}).

		$X0^+$			$A0^+$			B1		
v	**Band**	**MRCI**	**SO-MRCI**	**Exp**	**MRCI**	**SO-MRCI**	**Exp**	**MRCI**	**SO-MRCI**	**Exp**
1	1-0	181	186	203	133	114	117	57	86	89
	(1-0)	(181)	(186)	(203)	(133)	(114)	(117)	(57)	(86)	(89)
2	2-0	361	346	400	255	216	230	113	151	179
	(2-1)	(180)	(160)	(197)	(122)	(102)	(113)	(56)	(65)	(90)
3	3-0	541	518	595	368	311	341	164	216	263
	(3-2)	(180)	(172)	(195)	(113)	(95)	(111)	(51)	(65)	(84)
4	4-0	719	693	790	476	404	451	213	279	350
	(4-3)	(178)	(175)	(195)	(108)	(93)	(110)	(49)	(63)	(87)
5	5-0	897	870	977	583	494	560	260	341	431
	(5-4)	(178)	(177)	(187)	(107)	(90)	(109)	(47)	(62)	(81)
6	6-0	1074	1048	1169	687	583	665	306	403	513
	(6-5)	(177)	(178)	(192)	(104)	(89)	(105)	(46)	(62)	(82)
7	7-0	1252	1227	1367	789	670	774	350	463	587
	(7-6)	(178)	(179)	(198)	(102)	(87)	(109)	(44)	(60)	(74)
8	8-0	1429	1406	1557	889	755	875	394	524	665
	(8-7)	(177)	(179)	(190)	(100)	(85)	(101)	(44)	(61)	(78)
9	9-0	1606	1585	1744	988	839	978	437	585	739
	(9-8)	(177)	(179)	(187)	(99)	(84)	(103)	(43)	(61)	(74)
10	10-0	1782	1764	1925	1085	921	1079	479	643	807
	(10-9)	(176)	(179)	(181)	(97)	(82)	(101)	(42)	(58)	(68)
MAD	G(v)-G(0)	88	108	0	18	76	0	185	93	0
MAD	$\Delta G_{v+1/2}$	(16)	(14)	(0)	(5)	(16)	(0)	(33)	(28)	(0)

Table S3. Comparing the spectroscopic parameters obtained from spin-orbit corrected MRCI and spin-free MRCI levels

Method	**State**	**r_e(Å)**	**ω_e(cm^{-1})**	**$\omega_e x_e$(cm^{-1})**	**D_e(eV)**	**T_e(eV)**
SO-MRCI-DKH	$X0^+$	2.53	181.7	0.27	2.06	0
MRCI-DKH	$X^1\Sigma^+$	2.56	183	0.56	2.05	0
Exp.		2.496 [a]	198.22±0.11	0.512±0.002	2.06±0.10	0
SO-MRCI-DKH	$A0^+$	2.79	100	0.71	0.53	2.72
MRCI-DKH	$A^1\Sigma^+$	2.79	105.2	0.10	0.93	2.98
Exp.		-	115.7	0.74	0.48	2.72
SO-MRCI-DKH	B1	2.80	72.52	0.92	0.23	3.02
MRCI-DKH	$B^1\Pi$	2.85	47.09	0.1	0.19	3.72
Exp.		-	92.65	1.06	0.14	3.06

[a] The r_0 bond lengths of Au_2, Ag_2, Cu_2, CuAg, and CuAu are used to extract this value.[1]

Table S4. Vertical excitation energies calculated at r = 2.53Å at various levels of theory (non-relativistic, relativistic without spin-orbit and relativistic by considering spin-orbit coupling).

State	SO-MRCI-DKH	SO-MRCI	MRCI-DKH	MRCI
$X0^+$	0	0	0	0
$A0^+$	2.89	2.91	3.14	2.91
B1	3.16	5.71	3.89	6.41
MAD	0.13	1.42	0.63	1.77
	SO-TDDFT-ZORA	**SO-TDDFT**	**TDDFT-ZORA**	**TDDFT**
$X0^+$	0	-	0	0
$A0^+$	2.49	-	2.90	3.17
B1	2.64	-	3.30	4.79
MAD	0.32	-	0.21	1.09

Reference

1 Morse, M. D. Chemical Bonding in the Late Transition Metals: The Nickel and Copper Group Dimers. In *Advances in Metal and Semiconductor Clusters*; Duncan, M. A., Ed.; JAI Press: Greenwich, Conn., 1993; Vol. 1; pp 83.