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Relativistic effects on the ground state properties of group 1 and group 11 cyanides estimated from quantum chemical calculations

Dong-Ki Lee[a], Ivan S. Lim[a], Yoon Sup Lee[a,*], Gwang-Hi Jeung[b]

[a] *Department of Chemistry and School of Molecular Sciences (BK21), KAIST, 305-701 Daejeon, Republic of Korea*
[b] *Chimie Théorique, CNRS UMR6517, Université de Provence, Marseille, France*

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Abstract

All-electron scalar relativistic and nonrelativistic methods at various levels of the quantum chemical theory are employed to investigate spectroscopic constants for the cyanides of group 1 and group 11 metal atoms. The relativistic effect is small for the group 1 cyanides but much larger for the group 11 cyanides and increases as a function of the atomic charge. This can be explained in terms of the relativistic effects on the ionization potentials of metals and the atomic orbital contraction-dilations. The relativistic correction increases the covalent character of the bonding between the metal atom and the cyano radical in general. The spin-orbit effects on the spectroscopic properties are not so large except for the AuCN.

Keywords: Relativistic correction; Electron correlation; Natural population analysis; Spin-orbit effect; Ionicity and covalency

1. Introduction

Metal cyanide molecules have interested theoretical and experimental chemists because of their spectroscopic and dynamic properties. Model studies for the interaction of the cyanide group with metal surfaces are also possible in simple systems. The triatomic cyanides (MCN) made from a metal atom and a cyano radical can have two or three isomers which can be connected by a rotation of metal cation around CN anion [1]. There are many reports concerning the most stable form of the isomer and the resulting chemistry on the reaction coordinates [2–15]. Among closed shell metal cyanides, alkali metal (group 1) cyanides and the noble metal (group 11) cyanides have been studied most intensively. The group 1 cyanides are floppy molecules characterized by a small force constant about the M–CN bending mode while the group 11 cyanides exhibit more rigid structures [15]. The alkali cyanides are known to prefer the triangular geometry (T-form) whereas the noble metal cyanides prefer the linear MCN geometry. As discussed in our previous paper, the relativistic effects play an important role for cyanide molecules containing heavy elements. We feel that there is a considerable lack of investigation on this aspect, although the importance of relativistic effects on outer shells of heavy atoms such as Au was noted as early as 1975 by Desclaux and Kim and also by others [16,17].

In this work, we have used all-electron and pseudopotential (effective-core) methods to study the relativistic effects, namely the scalar effect and the spin-orbit effect. The electron correlation effect is also studied. The subject molecules are from KCN to FrCN in group 1 and from CuCN to AuCN in group 11, omitting LiCN and NaCN molecules for which the relativistic effects are unimportant.

2. Method of computation

For relativistic all-electron calculations, the ANO-RCC basis sets of Roos et al. [18] were used for the metals where scalar relativistic effects were accounted for using the second-order Douglas–Kroll Hamiltonian. For nonrelativistic calculations, these basis sets were totally decontracted and then recontracted using the coefficients obtained in nonrelativistic self-consistent calculations. The contraction scheme for the nonrelativistic basis sets was kept identical to the relativistic ones, which are: [21s16p5d4f/10s9p5d3f] for K, [23s19p11d4f/10s10p5d4f] for Rb, [26s22p15d4f/

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[*] Corresponding author at: Department of Chemistry and School of Molecular Sciences (BK21), KAIST, 373-1 Guseong-dong, Yuseong-gu, 305-701 Daejeon, Republic of Korea. Tel.: +82 42 869 2821; fax: +82 42 869 2810.
E-mail address: YoonSupLee@Kaist.Ac.Kr (Y.S. Lee).

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12s10p8d4f] for Cs, [28s25p17d12f/12s11p8d5f] for Fr, [21s15p10d6f4g2h/10s9p8d6f4g2h] for Cu, [21s18p13-d6f4g2h/10s9p8d6f4g2h] for Ag, and [24s21p15d11f4g2h/10s9p8d6f4g2h] for Au. Due to extensive computational cost with such large basis sets, the electron correlation was accounted for only at the second-order Møller-Plesset perturbation theory (MP2) level for all-electron calculations. This level of correlation treatment is believed to be sufficient as the primary purpose of the all-electron calculations here is to estimate relativistic effects from the comparison of the relativistic result with the corresponding nonrelativistic one. For the cyano radical, Gaussian type orbitals (GTOs), 13s8p2d for C and 12s7p3d for N, were used without contraction to make the atomic basis functions for both atoms [15]. These extended atomic basis sets were optimized to describe simultaneously the covalent and ionic configurations and the ground and excited states at molecular level. For the MP2 calculations, all electrons were explicitly correlated.

We carried out the geometry optimization at the Hartree-Fock (HF) and the MP2 level followed by harmonic vibrational frequency analysis. The anharmonic corrections were neglected in this study. For this the Molpro program package was used [19]. The molecular orbitals were further analyzed using the natural bond orbital (NBO) [20] program implemented in Gaussian 03 [21].

The spin-orbit effects were obtained from pseudopotential calculations using two-component spin-orbit pseudopotentials (SOPP) and spin-averaged relativistic pseudopotentials (ARPP). Comparisons are made to the all-electron results. For the group 1 metals, we employed small-core (nine-valence-electrons) energy-consistent pseudopotentials and corresponding basis sets of Lim et al. [22] while for the group 11 metals small-core (nineteen-valence-electrons) energy-consistent pseudopotentials and the valence basis sets of Figgen et al. were used [23]. For the calculations including spin-orbit effects were carried out with NWChem program package [24].

The three components of the dipole moment vector and the electrical neutrality of the triangular molecule were used to obtain the effective point charges centered at the nuclei. For the linear MCN molecules, the effective charges of slightly bent geometries around the equilibrium geometry were extrapolated according to the parabolic fitting.

3. Results and discussion

Optimized equilibrium geometries and harmonic vibrational frequencies for the group 1 and the group 11 metal cyanides are listed in Tables 1 and 2. These data are obtained at the nonrelativistic (NR) and scalar relativistic Douglas–Kroll (DK) level. The relativistic effect shortens the distance between the metal atom and CN but leaves the C–N distance little changed as can be seen in Table 1. The electron correlation effect to molecular geometries at the MP2 level is qualitatively consistent to those of the coupled-cluster level [15]. The relativistic effect increases the ω_1 and the ω_2 frequencies slightly (mainly the two modes of vibration involving the metal–CN bond) and decreases the ω_3 frequency (mainly the C–N stretching) for the alkali complexes but increases all frequencies for the noble metal complexes except for the ω_3 of CuCN as can be seen in Table 2. The correlation effects on the harmonic vibrational frequencies vary between the nonrelativistic case and the scalar relativistic case and molecule to molecule, so no general conclusions can be drawn from those tables in this regard. In addition, relativistic and electron correlation effects are not additive at all for the frequencies.

Table 1
Molecular geometries of the group 1 and the group 11 metal cyanides calculated with the nonrelativistic (NR) and the scalar relativistic Douglas–Kroll (DK) methods

	R(M–C)	R(C–N)	$\angle$(M–C–N)
KCN			
NR(HF)	2.907	1.151	60.234
DK(HF)	2.905	1.151	60.241
Δ_R(HF)	−0.002	0.000	0.007
NR(MP2)	2.696	1.185	69.983
DK(MP2)	2.693	1.185	70.000
Δ_R(MP2)	−0.003	0.000	0.017
RbCN			
NR(HF)	3.073	1.151	59.334
DK(HF)	3.062	1.151	59.531
Δ_R(HF)	−0.011	0.000	0.197
NR(MP2)	2.840	1.185	70.409
DK(MP2)	2.828	1.185	70.550
Δ_R(MP2)	−0.012	0.000	0.141
CsCN			
NR(HF)	3.302	1.152	55.755
DK(HF)	3.274	1.152	56.683
Δ_R(HF)	−0.028	0.000	0.928
NR(MP2)	3.022	1.186	69.082
DK(MP2)	2.999	1.186	69.703
Δ_R(MP2)	−0.023	0.000	0.621
FrCN			
NR(HF)	3.426	1.153	53.161
DK(HF)	3.323	1.152	57.060
Δ_R(HF)	−0.103	−0.001	3.899
NR(MP2)	3.114	1.186	68.249
DK(MP2)	3.028	1.186	70.927
Δ_R(MP2)	−0.086	0.000	2.678

	CuCN		AgCN		AuCN	
	R(M–C)	R(C–N)	R(M–C)	R(C–N)	R(M–C)	R(C–N)
NR(HF)	1.965	1.136	2.216	1.137	2.283	1.137
DK(HF)	1.938	1.136	2.139	1.136	2.004	1.132
Δ_R(HF)	−0.027	0.000	−0.077	−0.001	−0.279	−0.005
NR(MP2)	1.805	1.173	2.059	1.173	2.119	1.173
DK(MP2)	1.779	1.173	1.968	1.172	1.864	1.172
Δ_R(MP2)	−0.026	0.000	−0.091	−0.001	−0.255	−0.001

Bond lengths are in Å and bond angles in degrees.

The M–CN bond length of the T-shaped group 1 cyanides increases monotonically with increasing nuclear charge of the metal at both the nonrelativistic and the scalar relativistic cases. In spite of a large relativistic effect of Fr [25] shown in atomic and some molecular properties [22,26,27], this monotonic trend in the bond lengths of cyanide complex is interesting. The cyanide complexes are not the only molecular species which show such trend. The alkali fluorides studied by Kello and Sadlej showed no

Table 2
Harmonic vibrational frequencies (cm^{-1}) of the group 1 and the group 11 metal cyanides calculated with the nonrelativistic (NR) and the scalar relativistic Douglas–Kroll (DK) methods

	ω_2	ω_1	ω_3
KCN			
NR(HF)	112.45	307.00	2311.81
DK(HF)	114.55	307.33	2310.29
Δ_R(HF)	2.10	0.33	−1.52
NR(MP2)	172.65	298.04	1984.13
DK(MP2)	173.90	298.59	1982.39
Δ_R(MP2)	1.25	0.55	−1.74
RbCN			
NR(HF)	102.85	262.84	2310.89
DK(HF)	106.08	264.05	2309.33
Δ_R(HF)	3.23	1.21	−1.56
NR(MP2)	159.68	252.22	1983.02
DK(MP2)	163.84	253.64	1980.90
Δ_R(MP2)	4.16	1.42	−2.12
CsCN			
NR(HF)	89.92	242.43	2306.77
DK(HF)	94.44	243.69	2306.16
Δ_R(HF)	4.52	1.26	−0.61
NR(MP2)	137.71	233.77	1981.47
DK(MP2)	143.31	234.83	1979.32
Δ_R(MP2)	5.60	1.06	−2.15
FrCN			
NR(HF)	83.93	232.15	2304.29
DK(HF)	94.60	236.05	2306.24
Δ_R(HF)	10.67	3.90	1.95
NR(MP2)	127.45	221.22	1981.63
DK(MP2)	147.97	228.51	1977.94
Δ_R(MP2)	20.52	7.29	−3.69
CuCN			
NR(HF)	227.96	399.49	2457.53
DK(HF)	235.46	410.32	2459.95
Δ_R(HF)	7.50	10.83	2.42
NR(MP2)	227.12	495.84	2086.49
DK(MP2)	256.73	510.90	2083.97
Δ_R(MP2)	29.61	15.06	−2.52
AgCN			
NR(HF)	187.57	329.83	2444.80
DK(HF)	211.72	353.27	2454.89
Δ_R(HF)	24.15	23.44	10.09
NR(MP2)	177.92	385.03	2080.54
DK(MP2)	247.60	428.76	2086.44
Δ_R(MP2)	69.68	43.73	5.90
AuCN			
NR(HF)	183.42	309.68	2445.12
DK(HF)	287.60	418.89	2485.87
Δ_R(HF)	104.18	109.21	40.75
NR(MP2)	176.64	366.43	2079.41
DK(MP2)	298.67	524.55	2091.50
Δ_R(MP2)	122.03	158.12	12.09

contraction in the bond length from CsF to FrF [28]. Dyall and Partridge also did not see any drastic change with incorporation of the relativistic effects in the alkali fluorides [29], which was attributed to the ionic nature of the molecules.

In contrast, the M–C distance of the group 11 metal cyanides (linear) shows the regularly increasing trend for the CuCN, AgCN and AuCN suite in nonrelativistic calculation but does not so (the M–C distance of AgCN is larger than that of AuCN) for the relativistic calculation as can be seen in Table 1. Similar irregularity can be seen for the ω_1 and the ω_2 frequencies in Table 2. The shortening of the M–CN bond length from Ag–CN to Au–CN correlates with the increasing frequencies. The rather inconspicuous anomaly in the ω_2 mode for the group 1 metal cyanides for the CsCN and FrCN suite is due to the relativistic effect as revealed by comparing the nonrelativistic and the scalar relativistic all-electron results at the HF level (Table 2). The study on metal fluorides by Dyall [29] did not show any large relativistic effects even for the molecule containing heavy elements.

In the case of cyanide complex, there is a small but important valence s-character present for the M–CN bond as well as the more predominant p-character. The NBO population for the valence s shell are at the nonrelativistic level, 0.0179, 0.0146, 0.0104, and 0.0090 and at the DK level, 0.0182, 0.0155, 0.0121, and 0.0140 for the K, Rb, Cs, and Fr complexes, respectively. When we look into these two cases, we can infer that relativistic correction to the population number is consistent with the change in the harmonic frequencies of the ω_2 mode. The extent of change due to relativistic effects is maximized for the Fr molecule. However, the change is not enough to bring about an anomaly in the overall trend to a degree comparable to that for strongly covalent molecules. These results are plausible considering smaller electronegativity of CN than that of F [30]. The dipole moment is more sensitive to the relativistic effects than the bond distances resulting in an inverse trend in the dipole moment for the CsCN and FrCN. Similar trend was discussed by Kello and Sadlej for the case of fluorides [28], also ionic complexes.

If we compare Tables 1 and 2, we see that the normal modes of vibration about the metal, namely the ω_2(bending) and the ω_1(stretching), have inverse relationship to the M–CN bond length in terms of relativistic correction. For the group 1 cyanides the ω_2 mode shows larger increase in comparison with the bond length contraction, which means that bending is more sensitive to the topological effect [31] of the molecular potential energy surface.

For the M–CN bond lengths and the harmonic vibrational frequencies, the relativistic effect and the electron correlation effect change the observable to the same way (shortening bond length, increasing or decreasing frequencies), as in the group 11 hydride cases [32]. The relativistic corrections of dipole moments are larger in the correlated level (MP2) than in the uncorrelated level (HF). The relativistic effect of Au complex is incomparably large [25].

All group 1 metal cyanides have strong ionic character, as indicated by Clementi et al. [33], even though the effective charges of the metal atoms situating between 0.75 and 0.85 are not as large as that of the alkali metal fluorides. The CN complexes of the noble metal atoms have comparatively less effective charges. Table 3 shows the dipole moments and the effective charges of the metal cyanides. It can be seen that the effective charges of the metals atoms decrease according to the order K → Fr and Cu → Au in agreement with the commonly

Table 3
Dipole moments and the effective charges (a.u.) of the group 1 and the group 11 cyanides at calculated with the nonrelativistic (NR) and the scalar relativistic Douglas–Kroll (DK) methods

XCN	Method	Dipole moment	Q(M)	Q(N)	Q(C)
KCN	NR(HF)	4.308	0.853	−0.415	−0.438
	DK(HF)	4.303	0.852	−0.415	−0.437
	NR(MP2)	4.021	0.829	−0.348	−0.481
	DK(MP2)	4.014	0.828	−0.348	−0.480
RbCN	NR(HF)	4.487	0.838	−0.402	−0.436
	DK(HF)	4.465	0.837	−0.401	−0.436
	NR(MP2)	4.180	0.815	−0.338	−0.477
	DK(MP2)	4.151	0.812	−0.337	−0.475
CsCN	NR(HF)	4.627	0.808	−0.381	−0.427
	DK(HF)	4.603	0.809	−0.382	−0.427
	NR(MP2)	4.267	0.783	−0.321	−0.462
	DK(MP2)	4.243	0.783	−0.321	−0.462
FrCN	NR(HF)	4.672	0.789	−0.370	−0.419
	DK(HF)	4.590	0.793	−0.370	−0.423
	NR(MP2)	4.288	0.764	−0.310	−0.454
	DK(MP2)	4.179	0.761	−0.310	−0.451
CuCN	NR(HF)	3.417	0.726	−0.338	−0.388
	DK(HF)	3.339	0.715	−0.336	−0.379
	NR(MP2)	2.849	0.659	−0.272	−0.387
	DK(MP2)	2.747	0.641	−0.267	−0.374
AgCN	NR(HF)	3.814	0.734	−0.347	−0.387
	DK(HF)	3.565	0.702	−0.339	−0.363
	NR(MP2)	3.199	0.652	−0.281	−0.371
	DK(MP2)	2.913	0.623	−0.269	−0.354
AuCN	NR(HF)	3.845	0.723	−0.343	−0.380
	DK(HF)	2.965	0.609	−0.307	−0.302
	NR(MP2)	3.200	0.646	−0.276	−0.370
	DK(MP2)	2.264	0.489	−0.246	−0.243

Table 4
Comparison of the equilibrium geometries of the group 1 and the group 11 metal cyanides calculated with different methods (in Å and degrees)

	R(M–C)	R(C–N)	∠(M–C–N)
KCN			
MP2[a]	2.693	1.185	70.000
CCSD(T)[b]	2.725	1.180	69.090
B3LYP[a]	2.758	1.171	66.928
Exp[c]	2.723	1.171	68.900
RbCN			
MP2[a]	2.828	1.185	70.550
CCSD(T)[b]	2.858	1.180	69.242
B3LYP[a]	2.903	1.171	66.292
Exp[c]			
CsCN			
MP2[a]	2.999	1.186	69.703
CCSD(T)[b]	3.032	1.181	68.182
B3LYP[a]	3.110	1.171	63.463
Exp[c]			
FrCN			
MP2[a]	3.028	1.186	70.927
CCSD(T)[b]	3.087	1.181	69.229
B3LYP[a]	3.165	1.171	64.254
Exp[c]			

	CuCN		AgCN		AuCN	
	R(M–C)	R(C–N)	R(M–C)	R(C–N)	R(M–C)	R(C–N)
MP2[a]	1.779	1.173	1.968	1.172	1.864	1.172
CCSD(T)[b]	1.837	1.165	2.028	1.166	1.918	1.165
B3LYP[a]	1.825	1.157	2.030	1.156	1.930	1.155
Exp[c]	1.829	1.162				

[a] This work; DKMP2 for MP2; ECP/B3LYP for B3LYP.
[b] ECP/CCSD(T). See Ref. [15].
[c] For KCN see Ref. [38]. For CuCN see Ref. [39].

admitted electronegativity scale. The relativistic effect does not change the dipole moment and the effective charge significantly for the alkali–CN complexes and the CuCN, but it reduces both of them largely in the AgCN and AuCN as can be seen in Table 3.

To understand the electron correlation effect to the molecular structure and the vibrational frequencies, three different methods were compared: the MP2 method, the coupled-cluster singles-and-doubles with noniterative triples (CCSD(T)) method, and the density functional theory (DFT) using a hybrid functional B3LYP. The result is summarized in Tables 4 and 5. The MP2 method tends to underestimate the M–CN bond length and overestimate the C–N bond length in comparison with the ECP/CCSD(T) method, as in some previous reports [5,7]. In contrast, the ECP/DFT calculations show the opposite tendency in comparison with the ECP/CCSD(T) results. For the group 11 complexes (rigid linear) the ECP/DFT result shows better agreement with the ECP/CCSD(T) result and available experimental data than for the group 1 cyanides (floppy T-form). A previous study on alkaline-earth dihydrides also proved such tendency of the DFT [34]. Among harmonic vibrational frequencies, the bending frequency ω_2 and the stretching frequency ω_3 show a noticeable sensitivity to different level of electron correlation. It is peculiar that the bending frequencies of the group 1 cyanides at the ECP/DFT level are underestimated in comparison to those of all-electron MP2 and ECP/CCSD(T). The largest deviation of bond angles of ECP/DFT is estimated to contribute to this discrepancy. For more rigid group 11 cyanides, sensitivity of the bending mode is also applied. In comparing the ECP/DFT data with the ECP/CCSD(T) data, we can check that differences of the bending frequencies (ω_2) are not negligible whereas the stretching frequencies (ω_1) are in good agreement. The MP2 ω_1 values also show some deviations from the ECP/CCSD(T) values. However, the MP2 gives about the same bending frequencies as the ECP/DFT values. Our data do not lead to a general conclusion about the relationship between the bond length and the stretching frequency because two factors should be considered, the potential energy surface and the reduced mass. The accuracy of the calculated spectroscopic properties is certainly related to the level of the electron correlation effect included in each method, but we cannot derive a general tendency in this regard either.

The chemical bonding between the metal atom and the cyano radical is of ionic type, one electron of the metal being found around the cyano radical in most of the time. So the resulting bond can be described as a metal atom cation and a cyanide anion (M^+CN^-). The dipole moments and the effective charges in Table 3 show the ionic nature of the metal cyanides. Fig. 1

Table 5
Comparison of the harmonic vibrational frequencies (cm^{-1}) of the group 1 and the group 11 metal cyanides calculated with different methods

	ω_2	ω_1	ω_3
KCN			
MP2[a]	173.90	298.59	1982.39
CCSD(T)[b]	165.50	298.87	2047.91
B3LYP[a]	145.89	298.23	2120.35
Exp[c]	139.00	288.00	2050.00
RbCN			
MP2[a]	163.84	253.64	1980.90
CCSD(T)[b]	153.01	255.38	2047.94
B3LYP[a]	128.72	256.37	2119.83
Exp[c]			
CsCN			
MP2[a]	143.31	234.83	1979.32
CCSD(T)[b]	134.16	234.08	2046.59
B3LYP[a]	105.93	237.40	2117.82
Exp[c]			
FrCN			
MP2[a]	147.97	228.51	1977.94
CCSD(T)[b]	136.20	223.91	2045.45
B3LYP[a]	108.92	226.21	2118.36
Exp[c]			
CuCN			
MP2[a]	256.73	510.90	2083.97
CCSD(T)[b]	335.85	518.58	2189.52
B3LYP[a]	250.89	476.94	2249.42
Exp[c]		480.00	
AgCN			
MP2[a]	247.60	428.76	2086.44
CCSD(T)[b]	186.18	395.15	2168.11
B3LYP[a]	218.35	390.75	2249.54
Exp[c]		390.00	
AuCN			
MP2[a]	298.67	524.55	2091.50
CCSD(T)[b]	258.77	478.43	2179.32
B3LYP[a]	285.91	463.06	2256.92
Exp[c]			

[a] This work; DKMP2 for MP2; ECP/B3LYP for B3LYP.

[b] ECP/CCSD(T). See Ref. [15].

[c] For KCN see Ref. [40]. For CuCN and AgCN see Ref. [13].

shows the equiamplitude surface of the highest occupied molecular orbital (HOMO) of the group 1 cyanide complex. One factor determining the ionicity in this type of bonding is the ionization potential of the metal atom and the electron affinity of the electronegative part (CN). The ionization potentials of the alkali atoms are 4.3407 eV (K), 4.1771 eV (Rb), 3.8939 eV (Cs), and 4.0727 eV (Fr) [35]. The larger ionization potential of Fr than that of Cs can be explained as a relativistic effect. The ionization potentials of the noble metal atoms are 7.7264 eV (Cu), 7.5762 eV (Ag), and 9.2255 eV (Au), which show a much stronger relativistic effect of the gold atom in comparison with the silver atom [16,17]. The larger ionization potentials of the noble metal atoms in comparison with the alkali atoms should lead to the weaker ionic bonding in the MCN complexes of the former in comparison with the latter, as are supported by the effective charges in Table 3. The largest ionization potential of the gold atom among the metal atoms studied here is consistent with the smallest ionicity as is confirmed by Table 3, too.

The *n*s electron of the alkali atoms participate little in the chemical bonding because of the ionic nature as can be seen in the highest occupied molecular orbital (HOMO) of Fig. 1. In the noble metal complexes, however, one electron originally belonging to the metal atom spends still a significant amount of time around the metal atom although it is found around the CN more often. The extreme case is the AuCN calculated with the DK (MP2) method in Table 3 which gives the equal probably of finding the electron around the metal atom as around the CN group. The population analysis on the natural molecular orbitals resulting from the scalar relativistic Douglas–Kroll method gives the s-populations of the metal atom: 0.1992 for CuCN, 0.1769 for AgCN, and 0.4869 for AuCN. The corresponding values for the NR method are 0.1743, 0.1241, and 0.1341, respectively. These numbers are fully consistent with the ionization potentials of the corresponding atoms. In the case of the CN complexes of the alkali atoms, the orbital energy of the *n*s single electron and that of the $(n-1)$d closed subshell are close enough to make a facile sd-hybridization in the case of the noble metal atoms

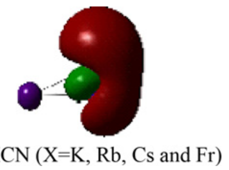

Fig. 1. Equiamplitude surfaces of the highest occupied molecular orbital (HOMO) of the alkali metal cyanides calculated with the scalar relativistic DK method.

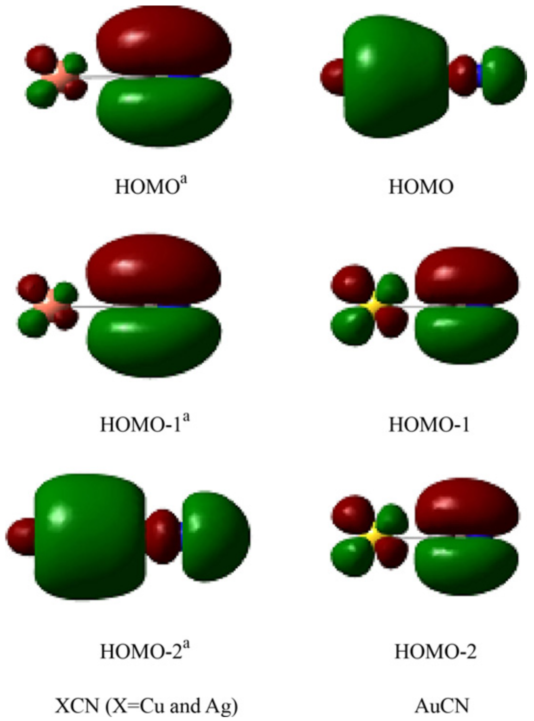

Fig. 2. Equiamplitude surfaces of the HOMOs of the noble metal cyanides calculated with the scalar relativistic DK method. Nonrelativistic AuCN is similar to AgCN. Degenerate π orbitals are shown as two orbitals.

[36]. In the gold atom case, the combination of the contraction of the 6s atomic orbital, the dilation of the 5d atomic orbital and the accompanying diminishment of the one electron orbital energy difference between these two atomic orbitals leads to an enhanced sd-hybridization. The HOMO shows mainly ionic character for CuCN and AgCN, but one can also see a substantial covalent bonding contribution in the case of AuCN (Fig. 2). It is also interesting to see in this figure that the electron donation from the metal to CN is mostly from sd_σ (M) to σ (CN). The molecular orbital representing this electron donation becomes HOMO for AuCN in the scalar relativistic calculations, but remains as HOMO-2 for all other cases, implying that large mixing of s-character is responsible for the increase of the orbital energy of this MO. Up to the HOMO, the back donation from CN to metal is not evident. The interaction between d_π (M) and π (CN) are weakly antibonding for all cases as shown in Fig. 2. The donation–backdonation scheme used for a weak covalent bonding [14] does not apply in the charge transfer complex as we could check in our result. For comparison, the second highest (HOMO-1) and the third highest (HOMO-2) orbitals are also reported in Fig. 2.

According to our separate calculation about the Au_2 molecule, about 2.52% of the d atomic orbital participates in the sd-hybridization, while it is 8.76% in the AuCN. This may originate from a strong perturbation of the s and d subshells in the proximity of a largely electronegative CN group. In spite of the ionic character of the MCN, the Au–C bond length contraction due to the relativistic effect seems to be surprising if we refer to the relationship between the Pauling electronegativity scale of the ligand and the relativistic bond contraction analyzed by Schwerdtfeger [31]. The 0.279 Å contraction indicated in Table 1 is closer to the 0.255 Å for AuH [32] (HF) than the 0.178 Å for AuF [37] (HF). This can be understood by Frenking's suggestion that AuCN can be better described by its smaller ionicity than CuCN and AgCN [14]. According to the effective charge analysis in Table 3, the covalent and ionic contributions should be about equal in the AuCN case.

Table 6
Calculated molecular geometries of the group 1 and the group 11 metal cyanides without (ARPP-HF) and with (SOPP-HF) the spin-orbit coupling (in Å and degrees)

	R(M–C)	R(C–N)	∠(M–C–N)
KCN			
ARPP	2.904	1.152	60.493
SOPP	2.904	1.152	60.460
Δso	0.000	0.000	−0.033
RbCN			
ARPP	3.060	1.152	59.528
SOPP	3.060	1.152	59.504
Δso	0.000	0.000	−0.024
CsCN			
ARPP	3.274	1.152	56.624
SOPP	3.274	1.152	56.541
Δso	0.000	0.000	−0.083
FrCN			
ARPP	3.333	1.152	57.176
SOPP	3.330	1.152	56.845
Δso	−0.003	0.000	−0.331

	CuCN		AgCN		AuCN	
	R(M–C)	R(C–N)	R(M–C)	R(C–N)	R(M–C)	R(C–N)
ARPP	1.935	1.135	2.137	1.136	2.002	1.132
SOPP	1.935	1.135	2.136	1.135	1.990	1.132
Δso	0.000	0.000	−0.001	−0.001	−0.012	0.000

Table 7
Calculated harmonic vibrational frequencies (cm^{-1}) of the group 1 and the group 11 metal cyanides without (ARPP-HF) and with (SOPP-HF) the spin-orbit coupling

	ω_2	ω_1	ω_3
KCN			
ARPP	113.60	306.46	2311.62
SOPP	113.94	307.04	2311.63
Δso	0.34	0.58	0.01
RbCN			
ARPP	103.82	264.95	2310.83
SOPP	104.02	265.18	2310.78
Δso	0.20	0.23	−0.05
CsCN			
ARPP	92.71	244.26	2308.30
SOPP	92.88	244.40	2308.12
Δso	0.17	0.14	−0.18
FrCN			
ARPP	93.58	233.98	2308.26
SOPP	92.59	235.93	2307.67
Δso	−0.99	1.95	−0.59
CuCN			
ARPP	235.17	412.09	2462.54
SOPP	235.02	412.54	2462.78
Δso	−0.15	0.45	0.24
AgCN			
ARPP	210.16	353.24	2457.41
SOPP	212.06	354.37	2458.10
Δso	1.91	1.13	0.69
AuCN			
ARPP	286.25	421.72	2489.99
SOPP	307.68	428.92	2491.93
Δso	21.43	7.20	1.94

Tables 6 and 7 display the spin-orbit effects of metal cyanides. The ARPP result is in good agreement with the scalar DK relativistic result of Tables 1 and 2, proving a reliability of the pseudopotentials used in this work. The spin-orbit effect is not large for the MCN molecules studied here. However, the AuCN shows a large spin-orbit effect. This is due to the increase of ds-hybridization for the molecule in the relativistic treatment. The spin-orbit coupling increases the ω_2 (bending) and ω_1 (stretching) frequencies and decreases the M–CN bond length.

4. Conclusions

We reported here the relativistic effect on the molecular properties of the alkali metal CN complexes and the noble metal–CN complexes: the bond lengths, the vibrational harmonic frequencies, the dipole moments and the effective charges. The relativistic effect is larger in the noble metal CN complexes than in the alkali metal CN complexes, and increase according to the atomic mass. There occurs a change of tendency in the properties between the Cs and Fr complexes and between the Ag and Au complexes. In particular, the AuCN shows very large relativistic effects, both the scalar effect and the spin-orbit coupling. The relativistic effects tend to decrease the ionicity of the $M^{+}CN^{-}$ bonding, which can be interpreted in terms of the augmentation of the metal atomic ionization potential due to the relativistic effect. The Au–CN bond shows a significant amount of covalency. The relativistic effects also increase the sd-hybridization for the noble metal CN complexes due to the contraction of the metal *n*s atomic orbital and the dilation of the metal $(n-1)$d atomic orbital, accompanied by the decrease of the one electron orbital energy difference between these two atomic orbitals. One important question remains: Why the noble metal complexes of CN are linear, whilst the alkali–CN complexes are triangular? Boldyrev et al. [13] have supposed that the linearity of the MCN molecule is mainly caused by the covalency of the chemical bond between M and CN. However, the Cu–CN and Ag–CN bonds are still largely ionic rather than covalent. One conclusion can be established though from our work that the linearity is not caused by the relativistic effect, nor caused by the electron correlation effect.

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References

[1] S.C. Farantos, J. Tennyson, J. Chem. Phys. 82 (1985) 800.
[2] M.L. Klein, J.D. Goddard, D.G. Bounds, J. Chem. Phys. 75 (1981) 3909.
[3] P.E.S. Wormer, J. Tennyson, J. Chem. Phys. 75 (1981) 1245;
R. Esser, J. Tennyson, P.E.S. Wormer, Chem. Phys. Lett. 89 (1982) 223.
[4] C.J. Marsden, J. Chem. Phys. 76 (1982) 6451.
[5] P.R. von Schleyer, A. Sawaryn, E.A. Reed, P. Hobza, J. Comput. Chem. 7 (1986) 666.
[6] J. Makarewicz, T.-K. Ha, Chem. Phys. Lett. 232 (1995) 497.
[7] S. Petrie, J. Phys. Chem. 100 (1996) 11581;
S. Petrie, PCCP 1 (1999) 2897.
[8] C.W. Bauschlicher Jr., Surf. Sci. 154 (1985) 70.
[9] C.J. Nelin, P.S. Bagus, M.R. Philpott, J. Chem. Phys. 87 (1987) 2170.
[10] I. Garcia Cuesta, A. Sanchez de Meras, I. Nebot-Gil, Chem. Phys. 170 (1993) 1.
[11] A. Veldkamp, G. Frenking, Organometallics 12 (1993) 4613.
[12] L. Bouslama, A. Daoudi, H. Mestdagh, C. Rolando, M. Suard, J. Mol. Struct.: Theochem 330 (1995) 187.
[13] A.I. Boldyrev, X. Li, L.-S. Wang, J. Chem. Phys. 112 (2000) 3627.
[14] O. Dietz, V.M. Rayon, G. Frenking, Inorg. Chem. 42 (2003) 4977.
[15] D.-k. Lee, I.S. Lim, Y.S. Lee, D. Hagebaum-Reignier, G.-H. Jeung, J. Chem. Phys. 126 (2007) 24433.
[16] J.P. Desclaux, Y.-K. Kim, J. Phys. B 8 (1975) 1177.
[17] P.S. Bagus, Y.S. Lee, K.S. Pitzer, Chem. Phys. Lett. 33 (1975) 408.
[18] B.O. Roos, V. Veryazov, P.-O. Widmark, Theor. Chem. Acc. 111 (2003) 345.
[19] H.-J.Werner, P.J. Knowles, R.D. Amos, A. Bernhardsson, A. Berning, P. Celani, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P.J. Knowles, T. Korona, R. Lindh, A.W. Lloyd, S.J. McNicholas, F.R. Manby, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, Molpro, Version 2002.1, A package of ab initio programs, Birmingham, UK, 2002.
[20] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, Gaussian 03, Revision B.03, Gaussian, Inc., Pittsburgh, PA, 2003.
[22] I.S. Lim, P. Schwerdtfeger, B. Metz, H. Stoll, J. Chem. Phys. 122 (2005) 104103.
[23] D. Figgen, G. Rauhut, M. Dolg, H. Stoll, Chem. Phys. 311 (2005) 227.
[24] T.P. Straatsma, E. Apra, T.L. Windus, M. Dupuis, E.J. Bylaska, W. de Jong, S. Hirata, D.M.A. Smith, M.T. Hackler, L. Pollack, R.J. Harrison, J. Nieplocha, V. Tipparaju, M. Krishnan, E. Brown, G. Cisneros, G.I. Fann, H. Fruchtl, J. Garza, K. Hirao, R. Kendall, J.A. Nichols, K. Tsemekhman, M. Valiev, K. Wolinski, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, M. Deegan, K. Dyall, D. Elwood, E. Glendening, M. Gutowski, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kobayashi, R. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, S. Niu, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Thomas, J. van Lenthe, A. Wong, Z. Zhang, NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.5, Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA, 2003.
[25] P. Pyykko, Chem. Rev. 88 (1988) 563.
[26] I.S. Lim, M. Pernpointner, M. Seth, J.K. Laerdahl, P. Schwerdtfeger, Phys. Rev. A 60 (1999) 2822.
[27] I.S. Lim, P. Schwerdtfeger, T. Sohnel, H. Stoll, J. Chem. Phys. 122 (2005) 134307.
[28] I. Miadokova, V. Kello, A.J. Sadlej, Mol. Phys. 96 (1999) 179.
[29] K.G. Dyall, H. Partridge, Chem. Phys. Lett. 206 (1993) 565.
[30] S.G. Bratsch, J. Chem. Educ. 65 (1988) 223.
[31] P. Schwerdtfeger, M. Dolg, W.H.E. Schwarz, G.A. Bowmaker, P.D.W. Boyd, J. Chem. Phys. 91 (1989) 1762.
[32] C.L. Collins, K.G. Dyall, H.F. Schaefer III, J. Chem. Phys. 102 (1995) 2024.
[33] B. Bak, E. Clementi, R.N. Kortzeborn, J. Chem. Phys. 52 (1970) 764.
[34] I.S. Lim, Y.S. Lee, J. Chem. Phys. 126 (2007) 104307.
[35] See Physical Reference Data from the NIST website (http://nist.gov/).

[36] P. Schwerdtfeger, P.D.W. Boyd, A.K. Burrell, W.T. Robinson, M.J. Taylor, Inorg. Chem. 29 (1990) 3593.
[37] J.K. Laerdahl, T. Saue, K. Faegri Jr., Theor. Chem. Acc. 97 (1997) 177.
[38] J.J. van Vaals, W.L. Meerts, A. Dymanus, J. Mol. Spectrosc. 106 (1984) 280.
[39] D.B. Grotjahn, M.A. Brewster, L.M. Ziurys, J. Am. Chem. Soc. 124 (2002) 5895.
[40] Z.K. Ismail, R.H. Hauge, J.L. Margrave, J. Chem. Phys. 57 (1972) 5137; Z.K. Ismail, R.H. Hauge, J.L. Margrave, J. Mol. Spectrosc. 45 (1973) 304; Z.K. Ismail, R.H. Hauge, J.L. Margrave, J. Mol. Spectrosc. 54 (1975) 402.