Comparative Study of Electron Correlation and Relativistic Effects in CuF, AgF, and AuF

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Spectroscopic and electric properties of the series of diatomic molecules FCu, FAg, and FAu are calculated using the coupled cluster CCSD(T) method and considering relativistic effects by the no-pair one-component Douglas−Kroll−Hess approximation. The correlation and relativistic effects in the FM series (M = Cu, Ag, Au) are compared with these effects in the AlM series. Differences in the bonding character and consequently also in molecular properties in FM and AlM are primarily due to different relativistic effects in both series. Relativity destabilized all bonds in the FM series but led to the increase of bond energy in all AlM diatomics. At the same time correlation effects were similar in all FM and AlM molecules, making all bonds considerably stronger. The different influences of relativistic effects on the bond energy are interpreted in traditional terms of electronegativities of constituent atoms supplemented by the comparative analysis of correlation and relativistic effects on electric properties in both the FM and the AlM series. The polarity of FM and AlM molecules is opposite and the dipole polarizabilities in the FM series are much lower than those in the AlM series.

I. Introduction

The series of FM molecules calculated in the present paper represents an extension of the two sets of diatomics investigated previously by Barysz, Sadlej and one of the present authors.[1,2] Both BM[1] and AlM[2] series (with M = Cu, Ag, Au) represent molecules with the same molecular orbital picture. Both form stable diatomic species in the $^1\Sigma$ ground state with the bonding primarily arising from a σ orbital formed by the 2p valence orbital of B or Al, respectively, and ns valence orbital of M. The BM series was investigated by both CASPT2[3] (complete active space calculation followed by the second-order perturbation treatment for the dynamical correlation) and the coupled cluster calculations, CCSD(T),[4] with the iterative solution for single and double excitations operators amplitudes accompanied by the noniterative calculation of the effect of triple excitation; see also ref 5. The AlM series was investigated at the CCSD(T) level. Relativistic effects were accounted for by using the Douglas−Kroll−Hess (DK) method[6] in its spin-averaged form[7] as implemented by Hess. Both correlation and relativistic effects reinforce the binding energy in BM and AlM, shorten the bond length, increase the harmonic vibrational frequency, and diminish the dipole polarizability (calculated only for AlM). At the same time, again, both correlation and relativistic effects lead to a change of polarity in AlM. The dipole moment of all AlM compounds at the equilibrium distance is negative at the SCF nonrelativistic (SCF−NR) level, less negative at the SCF−DK level and positive at the CCSD(T)−NR level. This change of polarity is further reinforced by relativistic effects. The positive sign corresponds to the polarity $Al^{(+)}M^{(-)}$ which means that relativity supports the charge transfer from Al to M. In the BM series these trends appear to be similar but are less transparently presented.

For the properties of the present series, FM, one can expect quite different behavior. On the basis of an excellent analysis by Pyykkö[8] extended further by pseudopotential investigations of Schwerdtfeger et al.[9] one can deduct that, in contrast to BM and AlM, the relativistic effect will weaken the binding energy and will show an opposite trend in the polarity of the FM series. This is quite interesting since, in the FM diatomics, their σ bonds are, as in the BM and AlM series, formed by the 2p valence orbital of F and the *n*s valence orbital of M.

The purpose of the present paper is to compare carefully CCSD(T) results obtained for FM with the AlM (and to a lesser extent BM) series. Also, a comparison to Schwerdtfeger's group results allows to compare the pseudopotential methods with results of all electron calculations. The discussion of differences in the bonding character in FM and AlM is the main objective of the paper. The comparison of dissociation energies and bond lengths of FM and AlM molecules will be accompanied by a comparison of their electric properties, namely dipole moments and dipole polarizabilities.

II. Computational Details

All results presented in this paper are all electron calculations with the contracted Gaussian−type (CGTO) basis of the size [10.6.4/5.3.2] for the fluorine atom and [16.12.6.4/9.7.3.2], [19.15.9.4/11.9.5.2], and [21.17.11.9/13.11.7.4] for Cu, Ag, and Au atoms, respectively. Different contraction coefficients with the same exponents of Gaussian primitives were used for nonrelativistic and relativistic calculations. Nonrelativistic basis sets for F[10] and M[11] are denoted by the acronym PolM for a specific atom M, and relativistic basis sets, used in DK calculations, are NpPolM basis sets for F[12] and M[13] respectively.

In all calculations $2s^2\,2p^5$ shells of F and $(n-1)p^6(n-1)d^{10}ns^1$ shells of M, i.e., altogether 24 electrons were correlated. The correlating effect from the $(n-1)s^2$ electrons was examined for FCu and FAg diatomics and was shown to be very small. To correlate $(n-1)\,s^2$ electrons for Au would mean that also the $4f^{14}$ shell needs to be explicitly correlated, since in Au 4f levels lie higher than its 5s level[13] with the DK−SCF wave function.

About 30 points have been calculated on potential energy curves for the present FM molecules and used in the calculation

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TABLE 1: Nonrelativistic (NR) and Relativistic Douglas−Kroll (DK) Equilibrium Bond Distances, Dissociation Energies,[a] and Harmonic Vibrational Frequencies of FCu, FAg, and FAu

	equilibrium bond distance (Å)			dissociation energy (eV)			ω_e (cm^{-1})		
	NR	DK	Δ[b]	NR	DK	Δ[b]	NR	DK	Δ[b]
CuF									
SCF	1.823	1.805	−0.018	2.53	2.48	−0.05	566.4	576.5	10.1
MBPT2	1.746	1.720	−0.026				622.7	644.9	22.2
CCSD	1.773	1.752	−0.021	4.06	4.04	−0.02	609.1	628.0	18.9
CCSD(T)	1.775	1.752	−0.023	4.08	4.04	−0.04	598.7	614.7	16.0
AgF									
SCF	2.072	2.034	−0.038	2.17	1.94	−0.23	473.4	491.5	18.1
MBPT2	2.035	1.990	−0.045				493.3	515.7	22.4
CCSD	2.047	2.004	−0.043	3.57	3.23	−0.34	488.7	508.5	19.8
CCSD(T)	2.046	2.004	−0.042	3.55	3.32	−0.23	486.2	505.1	18.9
AuF									
SCF	2.133	1.977	−0.156	2.04	1.34	−0.70	458.2	541.9	83.7
MBPT2	2.098	1.923	−0.175				479.0	583.1	104.1
CCSD	2.109	1.947	−0.162	3.30	2.79	−0.51	474.0	564.3	90.3
CCSD(T)	2.109	1.947	−0.162	3.39	2.93	−0.46	470.6	555.5	84.9

[a] CCSD(T)−DK basis set superposition error is 0.20 eV for CuF, 0.16 eV for AgF, and 0.32 eV for AuF; all data presented in Table 1 are uncorrected for BSSE. [b] The difference of DK and NR values.

of basic spectroscopic constants (r_e, D_e, ω_e, and $\omega_e x_e$). Electric properties, dipole moment (μ) curves, and dipole polarizabilities (α_e) for corresponding internuclear distances were calculated using the finite field method[14] as described in our previous work.[2] The external electric field was ±0.001 au, and the dipole moments and polarizabilities were calculated as first and second numerical derivatives, respectively. Computer programs used were the MOLCAS program[15] for the integral and SCF calculations, the Titan program[16] for the closed shell CCSD(T) calculations, and the ROHF CCSD(T) program developed in our laboratory[17] for the open shell fragments.

III. Results and Discussion

A. Spectroscopic Constants. Equilibrium bond distances, dissociation energies, and harmonic vibrational frequencies of FCu, FAg, and FAu obtained by the SCF, CCSD, and CCSD(T) methods are collected in Table 1. Both nonrelativistic (NR) and DK results are presented to estimate the importance of correlation and relativistic effects. In DK results the mixed correlation−relativistic effect is included. We will not discuss this last term separately since it was analyzed carefully in our previous papers.[1,2] We just stress that it is not negligible.

We observe large contribution of electron correlation in all properties, primarily in D_e. The pure electron correlation effect (a difference of CCSD(T)-NR and SCF−NR value) reinforces the bond and is 1.55 eV (FCu), 1.38 eV (FAg), and 1.35 eV (FAu), respectively. In fact it is very similar for all investigated valence isoelectronic species. This is quite analogous with similar differences[2] for AlCu (1.48 eV), AlAg (1.17 eV), and AlAu (1.17 eV). Analogous to this is also an observation that correlation effects are more important in FCu and AlCu than in other compounds that is related to a larger participation of the copper d orbitals in the binding. With ω_e we observe analogous trends. With the consideration of the electron correlation (at the CCSD(T)-NR level), ω_e is larger in comparison with its SCF value in all cases, by 32, 13, and 12 cm^{-1} for FCu, FAg, and FAu, respectively, and by 60, 29, and 16 cm $^{-1}$ in the corresponding AlM series. The equilibrium bond distance also provides quite regular behavior (shortening) due to the electron correlation.

Quite different is the situation with relativistic effects considered as a difference CCSD(T)−DK − CCSD(T)−NR. While it still holds that the equilibrium bond lengths decrease and ω_e relativistically increases for both FM and AlM series[2] (by 16, 19, and 85 cm^{-1}for FCu, FAg, and FAu, and by 15, 32, and 113 cm^{-1} for AlCu, AlAg, and AlAu, respectively), completely different behavior is observed with the dissociation energy: The bond is relativistically *destabilized* in the FM series but relativisticaly *stabilized* in the AlM series and also in the BM series. Consequently, the relativistic CCSD(T)−DK dissociation energy of AlAu becomes larger than that of FAu. This behavior is transparently visualized in Figure 1.

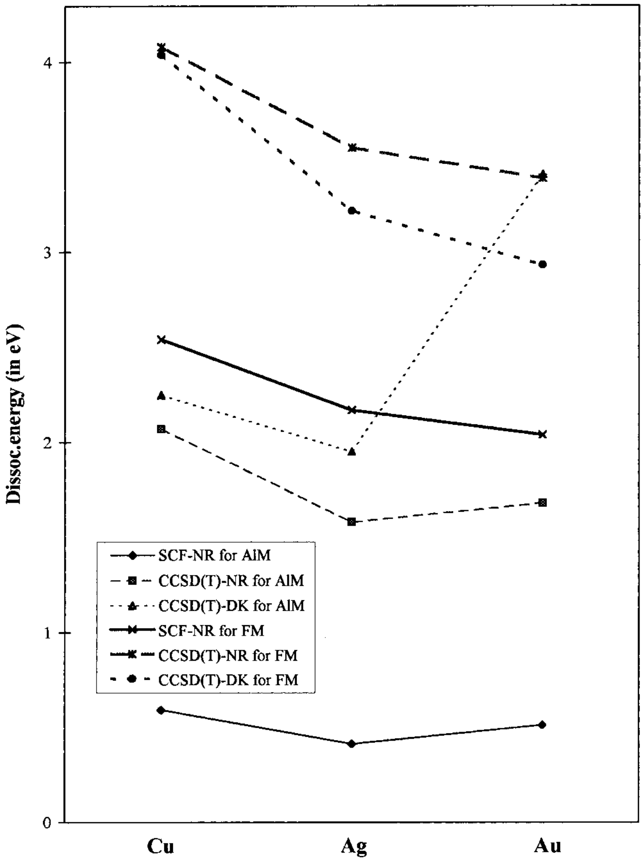

Figure 1. Comparison of correlation and relativistic effects on dissociation energies D_e of AlM and FM. Values for the AlM series are taken from ref 2 and unpublished results of Urban and Sadlej.

The explanation is based on an analysis of electronegativities of atoms which form our diatomic molecules, presented earlier

TABLE 2: Dipole Moments and Dipole Polarizabilities of FCu, FAg, and FAu[a]

	dipole moment[b](D)			polarizability (au)		
	NR	DK	Δ[c]	NR	DK	Δ[c]
			CuF			
SCF	−6.58	−6.41	0.17	14.70	14.98	0.28
MBPT2	−5.33	−5.07	0.26	21.12	21.74	0.62
CCSD	−5.61	−5.37	0.24	20.94	21.71	0.77
CCSD(T)	−5.54	−5.33	0.21	20.71	20.58	−0.13
			AgF			
SCF	−7.53	−7.10	0.43	18.95	19.95	1.00
MBPT2	−6.66	−6.09	0.57	25.53	27.06	1.53
CCSD	−6.78	−6.22	0.56	25.49	27.16	1.67
CCSD(T)	−6.63	−6.06	0.57	27.63	29.63	2.00
			AuF			
SCF	−7.53	−5.80	1.73	21.51	25.01	3.50
MBPT2	−6.66	−4.39	2.27	28.36	34.01	5.65
CCSD	−6.74	−4.62	2.12	28.66	33.26	4.60
CCSD(T)	−6.59	−4.40	2.19	31.02	35.86	4.84

[a] Dipole moments and dipole polarizabilities are calculated at equilibrium bond distances for a respective method, as presented in Table 1. [b] Vibrational averaging for the vibrational level $v = 0$ brings only a negligible change in the calculated results and is thus not presented. [c] The difference of DK and NR values.

by Schwerdtfeger et al.;[9] see also Pyykkö's investigations.[8] A much lower electronegativity of the Al atom in comparison to that of the fluorine atom leads also to a polarity in FM molecules different from that of AlM. More details on electric properties will be presented in the next section.

B. Electric Properties. Dipole moments and dipole polarizabilities for FM diatomics are collected in Table 2. The dipole moment curves are presented in Figure 2. All three molecules with all methods, including noncorrelated nonrelativistic SCF−NR show the same picture: The polarity is F$^{(-)}$M$^{(+)}$. This is in sharp contrast to AlM molecules where the polarity is opposite, Al$^{(+)}$M$^{(-)}$, at least when electron correlation is considered. Relativistic effects in the AlM series further support the negative charge at M, especially with AlAu. Also the shape of the dipole moment curves is quite different with FM and AlM, for FM being almost linear. In general, the polarity in AlM molecules shows a more complicated pattern than that for FM diatomics.

The F$^{(-)}$M$^{(+)}$ polarity is due to high electron affinity of the fluorine atom (−3.20 eV using NpPol basis set and the CCSD(T)−DK method), which is much higher than that of coinage metals (−1.20, −1.26, and −2.20 eV for Cu, Ag, and Au, respectively[18]). Since the ionization potential of M is relativistically enhanced by as much as by 0.23, 0.56 and 2.09 eV for Cu, Ag, and Au,[18] respectively, the charge shift from M to F is *reduced* due to relativity. This is connected with the fact that in this charge the shift involved is primarily *n*s electron and that its orbital is relativistically shrinked.[8,9] This weaker charge shift manifests itself in the decrease of the absolute value of the dipole moment in FM due to relativity, which is most pronounced in FAu, as expected. The decrease of the FM bond energy due to relativistic effects, as discussed in the previous part, is fully in line with the changes in the dipole moment.

Completely different trends due to relativity were observed in the AlM series.[2] In AlM bonds the charge transfer from Al to M is *relativistically supported* since the electron affinity of M relativistically increases, especially in the gold atom. This was confirmed in several papers, see, e.g., recent ones,[18,19] in which the same or related methods were applied as in the present work. Also, there is another difference, namely that FM bonds are very ionic—their dipole moments are much larger in absolute value than those in AlM. At the same time, the bond lengths in FM are significantly shorter than those in the corresponding AlM molecules. AlM bonds appear to be in fact more covalent. The linear dependence of the dipole moment on interatomic distance for FM in contrast to a more complicated shape of the dipole moment curves of AlM is fully in line with this interpretation. A slight deviation from linearity is only visible in the DK−CCSD(T) curve for FAu.

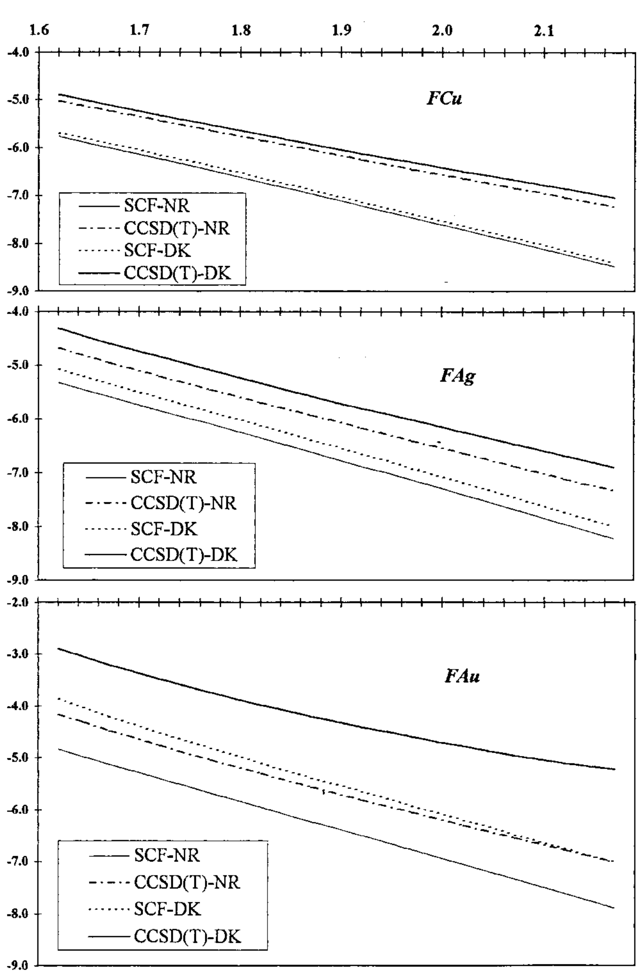

Figure 2. Dipole moment curves of FM: Correlation and relativistic effects. Dipole moments μ are in Debye and internuclear distances are in angströms.

Quite interesting are trends in polarizabilities of FM and their comparison with polarizabilities of AlM.[2] This is graphically shown in Figure 3. One observes a dramatic difference in polarizabilities in both series. First, polarizabilities of AlM are in general much larger, by a factor of 3.5−13, than those of FM. Second, polarizabilities of FM are much less influenced by correlation effects, at least when we speak about absolute values, than those of AlM. Also signs of changes of polarizabilities due to electron correlation are different in both series. Third, polarizabilities of FM are hardly influenced by relativistic effects, in contrast to those in the AlM series, and particularly in AlAu. It was found[2] that the polarizability of AlAu has decreased due to relativity from 179 au (CCSD(T)−NR) to 125 au (CCSD(T)−DK), i.e., by 54 au. The corresponding difference for FAu is an increase by 4.9 au, from nonrelativistic CCSD(T)−NR at 31.0 au to the relativistic CCSD(T)−DK value of 35.9 au. In other words, relativistic effects represent 43% of the final CCSD(T)−DK polarizability in AlAu but only 14% in FAu.

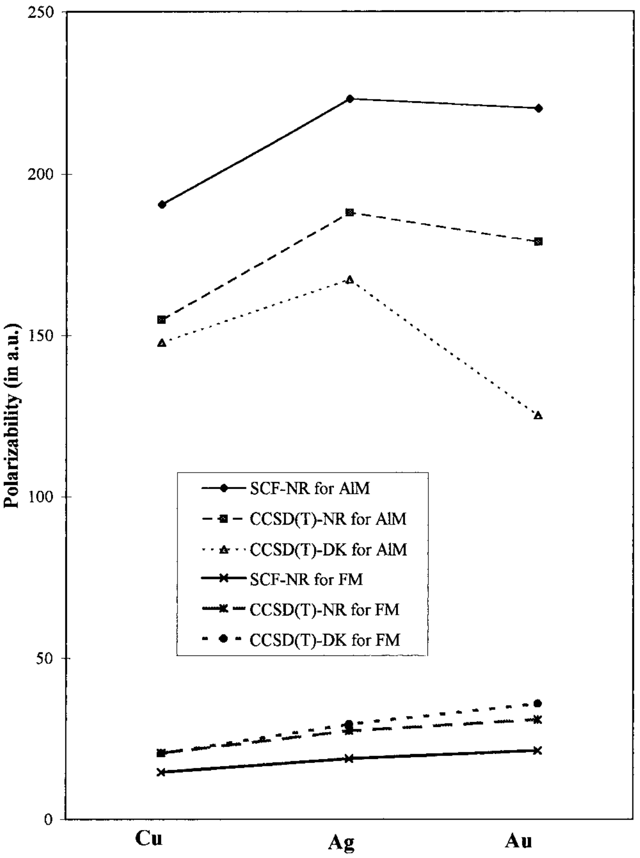

Figure 3. Comparison of correlation and relativistic effects on dipole polarizabilities α_e of FM and AlM. The dipole polarizabilities for FM are calculated at equilibrium bond distances for a respective method, as presented in Table 1. Values for the AlM series are taken from Table 3, ref 2.

TABLE 3: Comparison of CCSD(T) Dipole Polarizabilities (in au) of Ions Me$^+$ and F$^-$ with Molecular Polarizabilities of FMe

ionic pol	Cu^+	Ag^+	Au^+
NR	6.36	8.68	10.41
DK	6.62	9.28	12.21
sum[a]	$F^- + Cu^+$	$F^- + Ag^+$	$F^- + Au^+$
NR	16.78	19.10	20.83
DK	17.07	19.73	22.66
mol pol	FCu	FAg	FAu
NR	20.71	27.63	31.02
DK	20.58	29.63	35.86

[a] NR−CCSD(T) and DK−CCSD(T) polarizabilities of F^- are 10.42 and 10.45 au, respectively, calculated with $2s^22p^6$ electrons correlated.

TABLE 4: Spectroscopic and Electric Constants of FCu, FAg, and FAu Determined from Potential Energy Curves Obtained in Relativistic CCSD(T)−DK Calculations and Their Comparison with Experimental and Other Theoretical Data

	molecule		
property	$^{19}F^{63}Cu$	$^{19}F^{107}Ag$	$^{19}F^{197}Au$
r_e (Å)			
this work	1.752	2.004	1.947
exptl	1.745 [20]	1.983 [20]	
other theor results	1.721 [21][a] 1.749 [21][c] 1.730 [24][d] 1.723 [24][e] 1.773 [25][f] 1.725 [29][l]	1.993 [21][a] 2.032 [21][c] 1.996 [24][d] 1.994 [24][e] 2.000 [26][g] 1.977 [29][l]	1.938 [22][b] 1.946 [23][h] 1.939 [23][i] 1.899 [29][l]
ω_e (cm^{-1})			
this work	614.7	505.1	555.5
exptl	622.6(5) [20]	513.45 [20]	560 [30][j]
other theor results	653 [21][a] 659 [21][c] 655 [24][d] 652 [24][e] 632.6[25][f] 633 [29][l]	516 [21][a] 563 [21][c] 511 [24][d] 519[24][e] 574 [26][g] 521 [29][l]	539.4 [22][b] 525.3 [23][h] 538.6 [23][i] 590 [29][l]
$\omega_e x_e$ (cm^{-1})			
this work	3.65	3.04	2.25
exptl	3.95 [20]	2.59 [20]	1.0 [30][j]
other theor results	3.07 [25][f]	3.11 [26][g]	2.71 [22][b] 2.43 [23][h] 2.72 [23][i]
B_e (cm^{-1})			
this work	0.376	0.260	0.257
exptl	0.379 [20]	0.266 [20]	(0.24) [30][k] [23]
other theor results		0.261 [26][g]	0.259 [22][b] 0.256 [23][h] 0.259 [23][i]
D_e (D_0) (eV)			
this work	4.04 (4.01)	3.32 (3.29)	2.93 (2.89)
exptl	(4.4(2)) [20]	(3.6(4)) [20]	3.20 [27]
other theor results	3.81 [25][f] 4.61 [25][f]		3.10 (3.07) [22][b] (2.87) [23][h] (3.08) [23][i]
μ_e (in D)			
this work	−5.33	−6.06	−4.40
exptl	−5.7(7) [20]	−6.2(2) [20]	...
other theor results	−5.21 [25][f]		−4.88 [22][b] −5.68 [23][i]
α_e (au)			
this work	20.58	29.63	35.86
exptl	...	...	...
other theor results			34.32 [22][b]

[a] All electron (AE) DFT. [b] Average relativistic pseudopotential (ARPP) CCSD(T). [c] Pseudopotential (PP) DFT. [d] LDF (program DMol). [e] LDF (program DGauss). [f] CCSD(T). [g] Relativistic effective core potential (RECP) MRCI−MP2. [h] AE DK−MRCI. [i] ARPP QCISD(T). [j] Values for ω_e and $\omega_e x_e$ are unfortunately presented in ref 23 for the first excited state of FAu. Our computed value for $\omega_e x_e$, 2.25 cm^{-1}, is quite different from the experimental one, 1.0 cm^{-1}, and seems to agree instead with $\omega_e x_e$ for the first excited state (2.5 cm^{-1}) as presented in ref 30. Our theoretical value agrees fairly well with other theoretical results. [k] Assumed value. [l] Direct relativistic MP2 (26 electrons correlated).

An interesting view on the bonding character in FAu may be obtained by comparing molecular polarizabilities of molecules in this series with the sum of their ionic polarizabilities. This comparison is presented in Table 3 using CCSD(T) data. We observe immediately that the molecular polarizability is qualitatively similar to the sum of ionic polarizabilities at both nonrelativistic and relativistic levels. This demonstrates the ionic character of the $F^{(-)}M^{(+)}$ bonds. A similar comparison for the AlM series shows that the molecular polarizability is qualitatively similar to the sum of polarizabilities of $Al^{(+)}$ and $M^{(-)}$ (the polarizability of $Al^{(+)}$ is 24.1 au and that of $Au^{(-)}$ is 88.7 au with the CCSD(T)-DK method; the corresponding polarizability of the Al atom is 47.2 au, and the polarizability of Au with the same method is 35.6 au; the polarizability of AlAu is 125.0[2]). A more detailed analysis of correlation and relativistic effects in coinage metals is presented in refs 11 and 13. Note than our Au(^2S) atomic polarizability is slighty higher than the MVD (mass−velocity−darwin approximation) value reported in ref 11. Au^+ polarizability (see Table 3) is identical with that in ref 13; polarizabilities of Cu^+ and Ag^+ were recalculated with $(n-1)p^6 n-1)d^{10} ns^1$ electrons correlated, but differences from values reported previously[13] are marginal.

C. Comparison of Calculated Values with Available Experimental Data. The comparison of our values with experimental data and with the results of the other sophisticated theoretical calculations is presented in Table 4. For most properties the agreement with experiment is reasonable considering relatively small basis set PolM and NpPolM used in the present work. In short, the bond distances seem to be systematically overestimated: Our theoretical value is larger by 0.007 and 0.021 Å for FCu and FAg, respectively. For AuF it agrees to within 0.01 Å with most recent theoretical prediction in ref 22. Fairly good agreement with experiment is obtained for the harmonic vibration ω_e. The differences for FCu, FAg, and FAu are less than 10 cm^{-1}. In all cases our theoretical values are slightly underestimated in comparison to experimental values. Dissociation energies are significantly and systematically underestimated by our calculations in comparison to experiment. The difference is about 0.4 eV (i.e. 8.6%) for FCu, 0.3 eV (i.e. 8.8%) for FAg, and 0.27 eV (i.e. 8.4%) for FAu. We note that recent theoretical calculation of FCu by Hrušák et al.[25] predicts D_e 3.81 eV, i.e., 0.6 eV lower than the experimental value. They used the same correlated CCSD(T) method as was used in the present paper, but with a different number of correlated electrons and also with a different basis set. With a more extended basis set they estimate[25] $D_e = 4.61$ eV. They also noted dramatic problems with the use of an approximate CC method, namely QCISD(T), see also ref 28. Using QCISD(T) in calculations of the dipole moment led to a complete failure of this method due to the unbalanced approximate treatment especially of single excitations in the iterative solution of CC equations. In contrast to QCISD(T), a more rigorous CCSD(T) method gives dipole moments well within rather large error bars of experimental values for both FCu and FAg (theoretical values are systematically within the lower bound of experimental numbers). For FAu, the experimental value is not known to us. Our dipole moment for FCu agrees fairly well with the calculation of Hrušák et al.[25] The agreement with analogous pseudopotential calculation of FAu by Schwerdtfeger et al.[22] is less satisfactory (the difference is 0.48 D). Our dipole polarizability of FAu agrees very well with the pseudopotential CCSD(T) calculation by Schwerdtfeger et al.[22] Considering that our basis set, NpPol, is specifically designated for calculations of molecular electric properties and that in our calculation all electrons were explicitly considered, better agreement of our dipole moments with experiment is not surprising. This does not necessarily hold for dissociation energies and some other spectroscopic properties.

IV. Conclusions

The aim of the present work was to provide selected spectroscopic and electric properties for the series of diatomic molecules, FCu, FAg, and FAu. From the calculated data our dipole moments and also the dipole polarizabilities appear to be more reliable than spectroscopic constants, especially dissociation energies. This is connected with the fact that our basis sets, PolM and NpPolM, are especially designated[10] for nonrelativistic and relativistic calculations of electric properties. Polarizabilities cannot be compared to experiment since no data seem to be available. Theoretical calculations of polarizabilities were done only for AuF by Schwerdtfeger et al.[22]

The main goal of the present research was to use our data for the analysis of the bonding character and specifically the role of relativistic (and correlation) effects in the bond in the series of molecules. It was shown that the comparison of different role of relativistic effects in the present FM series and the AlM series calculated recently is particularly useful. The analysis has shown the usefulness of electric properties in such comparison. We have demonstrated that in the FM series the bond is ionic, in contrast to the AlM series in which the bonds appear to be more covalent.

The ionic character is in line with much larger dipole moment in FM molecules than in AlM molecules and with the almost linear dependence of the dipole moment on the bond length. At the same time the equilibrium bond lengths in FM molecules are shorter than those in AlM molecules. The polarities of the dipole moments are opposite with both series. This gives an additional look at the contribution of relativistic effects in bond energies that make FM bonds weaker and the AlM bonds stronger due to relativity. Since the electron transfer in FM goes from M to F and since relativistically stabilized ns electrons are mainly involved in bonds with the coinage atom, the weakening of the FAu bond by as much as 0.46 eV (see Table 1) is easily understood. The ionization potential of Au, in which relativistic effect is of course most pronounced, increases from the nonrelativistic CCSD(T)-NR value of 7.04 eV to the relativistic CCSD(T)−K value of 9.12 eV; see ref 18. In contrast to this we have observed a considerable increase of the bond strengths in AlAu (from 1.68 to 3.41 eV using CCSD(T)−NR and CCSD(T)−DK data, respectively) which is easily interpreted by the different charge shift, this time from Al to Au, which is relativistically enhanced due to the increase of the gold electron affinity by 1.07 eV.[18] This is fully in line with the characteristics of electric properties, namely dipole moments and dipole polarizabilities presented recently by Urban and Sadlej.[2] Thus, careful analysis of electric properties is very helpful as an alternative tool (together with the previously used[8,9] concept of electronegativities) in analyzing and understanding the bonding properties and particularly the influence of relativistic effects on the chemical bonds in our model systems.

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