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Ab initio study of $M\mathrm{Xe}_n^+$ (M=Cu, Ag, and Au; n=1,2)

Li Xin-Ying* and Cao xue
School of Physics and Electronics, Henan University, Kaifeng 475004, China

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The equilibrium geometries, vibrational frequencies, dissociation energies, and populations of the title species were studied at Hartree-Fock (HF), second-order Møller-Plesset (MP2), and coupled-cluster singles-doubles (triples) [CCSD(T)] levels. The electron correlation effects and relativistic effects on the geometry and stability were investigated at the CCSD(T) level. Both effects stabilize title species. The populations analyses show that M-Xe bonding is dominated by electrostatic interactions and the best theoretical estimate of the dissociation energies are 1.104 and 2.260 eV for AuXe^+ and AuXe_2^+, respectively. The Cu and Ag are weakly bonded to Xe compared to Au.

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I. INTRODUCTION

It was always considered that chemical compounds containing noble-gas elements could not be formed until the first noble-gas compound, xenon hexafluo-roplatinate $[\mathrm{Xe}^+(\mathrm{PtF}_6)^-]$, was reported 4 decades ago [1]. The existence of this kind of compound with noble-gas elements is of considerable significance to open up the fascinating field in physics and chemistry. Consequently, they are gradually discovered and well investigated in experiment and theory. What has attracted our interest is the Ng-M bonding in the noble-gas–noble-metal halides, $NgMX$ (Ng=Ar,Kr,Xe; M=Cu,Ag,Au; and X=F,Cl,Br), recently examined with a high-resolution Fourier transform microwave spectrometer [2–15]. Recently, Seidel and Seppelt demonstrated the existence of the $[\mathrm{AuXe}_4]^{2+}$ cation in crystal structure of the $\mathrm{AuXe}_4^{2+}(\mathrm{Sb}_2\mathrm{F}_{11}^{-1})_2$ compound. *Ab initio* calculations estimated a dissociation energy of approximately 200 Kcal/mol and a concentration of the positive charge was found mainly on the Xe atoms [16]. Pyykkö predicted the chemical bonds between noble gas and Au^+, an Au-Xe bond energy of up to 0.9 eV and bond length of 276 pm is reported [17]. The work is very important because it supports the concept that the noble-gas atoms can be directly bonded to the gold atom. In these species, the presence of chemical bonds between gold and xenon is in sharp contrast to the conventional behavior of noble-gas and noble-metal atoms, which are considered to be inert from the existing chemical intuitions. Such an Au-Xe bond would not have been viable if gold is considered as a truly noble metal and xenon a strictly noble gas. In fact, noble metal, such as gold, has a very rich and unusual chemistry with varying physicochemical properties due to the strong relativistic effects, which considerably decrease the size of the valence 6s orbital and lead to the expansion of the 5d orbital resulting in this kind of unusual behavior. Most recently, Belpassi reported a detailed and accurate study on the chemical bond between Au(I) and the noble gases [NgAu+(Ng=Ar,Kr,Xe)] by state-of-the-art all-electron fully relativistic Dirac-Coulomb CCSD(T) and discrete Fourier transform calculations with extended basis sets [18]. However, the theoretical investigations including geometrical structures, electronic structures, especially the roles of relativistic effects and electron correlation effects on noble-metal series $M\mathrm{Xe}^+$ (M=Cu, Ag, and Au) are less reported.

In the present research, the investigations of the $M\mathrm{Xe}_n^+$ (M=Cu, Ag, and Au, n=1,2) cations series are not only to understand the behavior of the systems under consideration, but also to give an insight into the nature of intramolecular bonding between noble-gas and noble-metal atoms. It would be meaningful and interesting to give a description of structures and properties of this class of compounds.

II. COMPUTATIONAL DETAILS

The relativistic pseudopotentials and the corresponding basis set SDD are used to describe the Xe atom [19]. The valence electrons of Xe atoms are composed of configuration $5s^2 5p^6$ and the basis set EXSDD for Xe stands for the expansion of SDD $(6s6p3d1f)/[4s4p3d1f]$ basis set in the following way. One set each of diffuse s, p, and d functions (exponents: 0.03, 0.02, 0.05) was added, the single f function was replaced by three f primitives (1.375, 0.55, 0.22), and one g function (0.55) was added, to yield an overall basis set of $(7s7p4d3f1g)/[5s5p4d3f1g]$ size [20]. The interactions in noble-gas atoms containing compounds often require the inclusion of very high angular momentum functions for accurate description [21], the present high momentum basis set EXSDD is proved to be sufficiently accurate and necessary to describe the interaction in our previous works [22].

The 19-valence electron relativistic and nonrelativistic pseudopotentials (RPP and NRPP) and the match basis set $[(8s7p6d)/[6s5p3d]]$ of Dolg [23,24] are employed for Au, Ag, and Cu atoms. Pyykkö found that two f-type polarization functions are desirable for the correct description of the interaction energy and the inclusion of an additional g function on gold has a sizable effect on the computed bond energy and also leads to a significant shrinking of $R_{\mathrm{Au\text{-}Xe}}$, therefore, two f functions (0.20 and 1.19 for Au, 0.22 and 1.72 for Ag, 0.24 and 3.7 for Cu) [25], and one g function (1.1077) [26] for Au are augmented to describe metallophilic attraction. Nonrelativistic pseudopotential for heavy elements are very useful for studying the relativistic effects in molecules

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*Corresponding author. lxying@henu.edu.cn

TABLE I. The optimized equilibrium distances (R_e/pm), vibrational frequencies (cm^{-1}), dipole moments (D), population and dissociation energies (D_e/eV) for MXe$^+$.

	Method	R_e	Frequency	Dipole	Pop. (M)	D_e	D_e(CP)[e]
CuXe$^+$	HF/RPP	270.8	126.3	5.64	0.702	0.520	0.505
	MP2/RPP	245.5	194.6	4.73	0.591	1.112	0.923
	CCSD(T)/RPP	249.5	185.8	4.87	0.607	1.075	0.888
	CCSD(T)/NRPP	262.7	155.1	5.50	0.663	0.765	0.658
AgXe$^+$	HF/RPP	302.8	82.9	5.30	0.757	0.331	0.326
	MP2/RPP	278.9	138.0	4.29	0.678	0.914	0.667
	CCSD(T)/RPP	276.0	134.0	4.39	0.685	0.871	0.646
	CCSD(T)/NRPP	298.6	97.9	5.47	0.758	0.443	0.353
AuXe$^+$	HF/RPP	285.4	94.5	2.32	0.613	0.501	0.499
	MP2/RPP	257.7	158.6	1.59	0.533	1.473	1.210
	CCSD(T)/RPP	262.8	147.8	1.70	0.542	1.345	1.104
	CCSD(T)/NRPP	311.7	77.8	3.99	0.787	0.378	0.303
	Previous	276.1[a]	145[a]			1.160[a]	0.910[a]
	work	257.4[b]	149[b]				1.305[b]
		260.9[c]	150.0[c]				1.327[c]
		256.2[d]					

[a] Reference [17].

[b] Reference [33].

[c] Reference [18].

[d] AuXe$^+$ distance in XeAuF [8], 258.5 in AuXeF [13], 265.0 in AuXeOH [13].

[e] BSSE corrected with counterpoise procedure.

by comparing the results obtained with their relativistic analogs.

The basis set superposition error (BSSE) is avoided by using counterpoise procedure (CP) of Boys and Bernardi [27].

The calculations were performed with the GAUSSIAN 03 W program package [28].

III. RESULTS AND DISCUSSION

A. Geometry

1. MXe$^+$

The optimized equilibrium distances, vibrational frequencies, dipole moments, Mulliken atomic charges on M atoms, and dissociation energies (D_e) for MXe$^+$ (M=Cu,Ag,Au) calculated at Hartree-Fock (HF), second-order Møller-Plesset (MP2), CCSD(T) theoretical levels with RPP and NRPP are given in Table I. The dissociation energies are referenced to the separated-atom limit consisting of ground-state xenon atom(s) and $M(I)s^0d^{10}$ ground states in the monovalent cation states. As can be seen from Table I, the results calculated at MP2/RPP and CCSD(T)/RPP levels are very close. The MP2 method is most commonly used in quantum chemical calculations, and is usually the first choice in considering the electron correlation effect. It typically obtains 90% of the total correlation energy [29,30]. The most accurate energy is generally obtained at the CCSD(T) level [31]. In fact, it was regarded that this complicated method could produce results in close agreement with full configuration interaction [32]. We, therefore, prefer the results of the CCSD(T)/RPP method to discuss the optimized geometry and stability of the systems.

For AuXe$^+$, the present equilibrium distance (R_e), 262.8 pm, is longer than the previous reported value of 276.1 pm, and dissociation energy [D_e and D_e(CP)], 1.345 and 1.104 eV, are greater than 1.160 and 0.910 eV reported in 1995 [17]; nevertheless, shorter than 257.4 pm in distance and 1.305 eV in dissociation energy [D_e(CP)] reported in 1998 by Pyykkö [33]. We notice that the present bond length is in good agreement with Belpassi's result of 260.9 pm, while there is a weaker stability than theirs (1.327 eV), the error may be resulted by the difference of the methods (RPP and full four-component DC Hamiltonian). We obtain almost identical vibrational frequencies with theirs. The results of AgXe$^+$ and CuXe$^+$ indicate that not only the Au can be directly bonded to the noble-gas atom xenon also the Ag and Cu have the same behavior with smaller dissociation energies. At the CCSD(T)/RPP theoretical level, the present best estimate of the dissociation energies are 0.646 and 0.888 eV, the equilibrium distances are 276.0 and 249.5 pm for AgXe$^+$ and CuXe$^+$, respectively. We notice that the equilibrium distances R_e ordering (longest to shortest) is CuXe$^+$ < AuXe$^+$ < AgXe$^+$, while the dissociation energies ordering (deepest to most shallow) is AgXe$^+$ < CuXe$^+$ < AuXe$^+$.

2. MXe$_2^+$

The higher total energy and imaginary frequencies of the bent structures indicate that it is an unstable structure. Herein, only the optimized geometry and the stability of lin-

TABLE II. The optimized equilibrium distances (R_e/pm), population and dissociation energies (D_e/eV) for $M\text{Xe}_2^+$.

	Method	R_e	D_e	$D_e(\text{CP})$[b]
CuXe_2^+	HF/RPP	270.7	0.983	0.957
	MP2/RPP	243.1	2.286	1.910
	CCSD(T)/RPP	247.8	2.175	1.812
	CCSD(T)/NRPP	261.3	1.533	1.296
AgXe_2^+	HF/RPP	302.9	0.629	0.620
	MP2/RPP	268.5	1.888	1.367
	CCSD(T)/RPP	272.2	1.777	1.305
	CCSD(T)/NRPP	296.1	0.891	0.689
AuXe_2^+	HF/RPP	281.4	1.027	1.007
	MP2/RPP	256.8	3.066	2.555
	CCSD(T)/RPP	262.2	2.729	2.260
	CCSD(T)/NRPP	309.7	0.760	0.595
	Pyykkö[a]	266.0		2.250

[a] Reference [17].

[b] BSSE corrected with counterpoise procedure.

ear structure were discussed and the results of $M\text{Xe}_2^+$ calculated at various theoretical levels are collected in Table II.

At CCSD(T)/RPP level, we arrive at the bond length of 262.2 pm and the dissociation energy [D_e(CP)] of 2.260 eV, which are in excellent line with the reported value of 266.0 pm and 2.250 eV of AuXe_2^+ [17]. The present vibrational frequencies of AuXe_2^+, 43.3(π_u), 119.1(σ_u), and 259.9(σ_u) cm^{-1}, match Pyykkö's results of 35(π_u), 120(σ_g), and 182(σ_u) very well [17]. The dissociation energies of AuXe_2^+ and CuXe_2^+, 1.305 and 1.812 eV, indicate that AgXe_2^+ and CuXe_2^+ can be formed as well as AuXe_2^+ but have smaller stabilities, the AgXe_2^+ has the most shallow potential well of the trimers. The R_e and D_e ordering of the trimers have the same behavior as its dimers. From dimer to trimer, at CCSD(T)/RPP theoretical level, the equilibrium distances, R_e, almost keep unchangeable, the decreases are 1.7, 3.8, and 0.6 pm, indicating that the existence of the other M atom should be a minor perturbation to the geometry, nevertheless, the stabilities are strongly enhanced as can be seen from the D_e collected in Tables I and II, the magnitude of trimer is almost 2 times its dimer, the ratios are 2.04, 2.02, and 2.02 for CuXe^+, AgXe^+, and AuXe^+, respectively. The noble-metal–noble-gas bonding is dominated by electrostatic interactions; by this criterion, the trimer can be simply regarded as two dimers.

B. Electron correlation and relativistic effects

The electron correlation effects play an important role in these systems and are accounted for using the coupled-cluster method with single and double excitation and a noniterative correction for triple excitations [CCSD(T)]. For $M\text{Xe}^+$, both HF and post-HF methods [MP2 and CCSD(T)] obtained the same electronic state ($^1\Sigma$ for $M\text{Xe}^+$ and $^1\Sigma_g$ for $M\text{Xe}_2^+$), the inclusion of electron correlation effects does not essentially change the electronic structures, but has a strong influence on geometrical structure and stability. At the CCSD(T)/RPP level, electron correlation effects contract the $M\text{Xe}^+$ distances R_e by 21.3, 26.8, and 22.6 pm, enhance the stabilities by 0.38, 0.32, and 0.65 eV for CuXe^+, AgXe^+, and AuXe^+, respectively. The dipole moment decreased and vibrational frequencies increased by electron correlation effects. The trimers have the same trend. The changes of structural parameters are due to the electronic reorganization when the electron correlations are included. The Mulliken total atomic charge analysis gives, for example, that the HF result is Au(0.613), and the CCSD(T) result is Au(0.542) for AuXe^+. The electron correlation effects transfer 0.07 charges from the Xe atom. The other systems have the same behavior.

In order to investigate the relativistic effects on the structure and stability, structural calculations were performed by using NRPP and RPP at the CCSD(T) theoretical level. A comparison of NRPP and RPP results reveals that relativistic effects have a strong influence on structural parameters and stability. At the CCSD(T) level, for $M\text{Xe}^+$, relativistic effects decrease the distances R_e by 13.2, 22.6, and 48.9 pm, enhance the stabilities by 0.23, 0.293, and 0.861 eV for CuXe^+, AgXe^+, and AuXe^+, respectively. The dipole moments decrease and vibrational frequencies increase. We noticed that, under the nonrelativistic condition, for the dimer, the equilibrium distances R_e ordering is $\text{CuXe}^+ < \text{AgXe}^+ < \text{AuXe}^+$ and that of dissociation energies is $\text{AuXe}^+ < \text{AgXe}^+ < \text{CuXe}^+$, this is in accord with the expected trend as one goes down the periodic table which normally leads to longer bond lengths and weaker interactions; while, when the relativistic effects are taken into account, the R_e ordering is $\text{CuXe}^+ < \text{AuXe}^+ < \text{AgXe}^+$ and D_e ordering is $\text{AgXe}^+ < \text{CuXe}^+ < \text{AuXe}^+$, the $M\text{Xe}^+$ is the most stable species of the dimer. The trimers have the same trend.

Generally, the NRPP predicts larger bond distance, larger dipole moment, and smaller dissociation energy as compared with the RPP at the same theoretical level. These regularities can be explained by the fact that the relativistic *s* orbitals are more stable than the corresponding nonrelativistic orbitals, and, on the contrary, relativistic *d* orbitals are more diffuse and less stable than the corresponding nonrelativistic ones.

Both electron correlation and relativistic effect stabilized the present species. The Au containing species is most stable and this stabilization is once again brought about by relativistic effects. As expected, these relativistic effects are much more pronounced for Au compared to Ag and Cu.

C. Population analyses

The first ionization energies of Cu, Ag, Au, and Xe are 7.726, 7.576, 9.225, and 12.13 eV, respectively. The difference of ionization potential (IP) between Xe and Au is not too large such that partial electron transfer can occur. It can be seen from Table I, at the CCSD(T)/RPP theoretical level, the charge transfers to the M^+ cation from the Xe atom are 0.393, 0.315, and 0.458 for CuXe^+, AgXe^+, and AuXe^+, respectively. Our result for AuXe^+ compare well with Belpassi's result of 0.43 [18]. The total CCSD(T) dissociation energy decrease from 1.104(AuXe^+) to 0.888(CuXe^+) and

0.646 eV ($AgXe^+$). The charge transfer becomes significant and total CCSD(T) dissociation energy becomes stronger with increasing of the IPs of M atoms ($Ag < Cu < Au$). It indicates that the M-Xe bonding is dominated by electrostatic interactions together with electron transfer from the ligand (Xe) to gold cation, the main future of the bond is a charge accumulation in the middle of the region between the Xe and Au nuclei [18].

However, under the nonrelativistic condition [CCSD(T)/NRPP level], the charge transfers are 0.337($CuXe^+$), 0.242($AgXe^+$), and 0.213($AuXe^+$), the total CCSD(T) dissociation energy increases from 0.303($AuXe^+$) to 0.353($AgXe^+$) and 0.658 eV ($CuXe^+$). The ordering of the nonrelativistic IPs of the M atom ($Au < Ag < Cu$) results in the change of charge transfer and dissociation energy.

From Table I we can see, for $AuXe^+$, the Mulliken populations are 0.613, 0.542, and 0.787 at the HF/RPP, CCSD(T)/RPP, and CCSD(T)/NRPP levels, there are considerable changes when the electron correlation and relativistic effect are included, the electronic reorganization results in the changes of structural parameters (see Sec. III B), and both changes bring on the decrease of the dipole moment and enhanced stability.

The total CCSD(T) dissociation energy decreases from 1.104 to 0.303 eV if relativistic effects are omitted for $AuXe^+$. This is not surprising. The calculated relativistic and nonrelativistic (RPP and NRPP) ionization potentials of Au are 8.998 and 7.023 eV, respectively. Relativistic effects increase IP of gold by 1.975 eV. Other recent calculations of the same increase give 2.105 [34] and 2.01 eV [35], respectively. While the same increase of Cu and Ag are 0.434 and 1.025 eV, respectively. Relativistic effects significantly stabilize the 6s orbital of the gold atom by about 2 eV, while these effects are almost negligible for copper and silver, being roughly proportional to the square of nuclear charge. As a consequence, not only does the ionization energy of atomic gold increase due to relativity but the 6s orbital also becomes much more electrophilic as compared to the 4s and 5s orbitals of Cu and Ag, respectively.

The IP of the ligand (Xe) may serve as a characteristic parameter for the amount of electron transfer from the ligand to the metal. Due to the electrophilicity of the 6s orbital of Au^+, however, interactions involving partial electron transfer from the ligand (Xe) to gold become significant resulting in an increase of covalent bonding in gold(I) complexes as the lower is the ionization energy of the ligand.

IV. CONCLUSION

The calculated results of MXe_n^+ (M=Cu, Ag, and Au, $n=1,2$) show that these species have linear structures ($n=2$). The population analyses show that the M-Xe bonding is dominated by electrostatic interactions; more charge transfer occurred for $AuXe_n^+$. The best theoretical estimate of the energies are 1.104 and 2.260 eV for $AuXe^+$ and $AuXe_2^+$, respectively; the Cu and Ag are weakly bonded compared to Au. From dimer to trimer, the equilibrium distances M-Xe nearly do not change. The electron correlation and relativistic effects have strong influence on the geometries and stabilities; they shorten the bond length, increase the vibrational frequencies, and thus enhance the stability.

[1] N. Bartlett, Proc. Chem. Soc., London **1962**, 218 (1962).
[2] C. J. Evans and M. C. L. Gerry, J. Chem. Phys. **112**, 1321 (2000).
[3] C. J. Evans and M. C. L. Gerry, J. Chem. Phys. **112**, 9363 (2000).
[4] C. J. Evans, A. Lesarri, and M. C. L. Gerry, J. Am. Chem. Soc. **122**, 6100 (2000).
[5] C. J. Evans, D. S. Rubino, and M. C. L. Gerry, Phys. Chem. Chem. Phys. **2**, 3943 (2000).
[6] L. M. Reynard, C. J. Evans, and M. C. L. Gerry, J. Mol. Spectrosc. **206**, 33 (2001).
[7] N. R. Walker, L. M. Reynard, and M. C. L. Gerry, J. Mol. Struct. **612**, 109 (2002).
[8] S. A. Cooke and M. C. L. Gerry, J. Am. Chem. Soc. **126**, 17000 (2004).
[9] S. A. Cooke and M. C. L. Gerry, Phys. Chem. Chem. Phys. **6**, 3248 (2004).
[10] J. M. Thomas, N. R. Walker, S. A. Cooke, and M. C. L. Gerry, J. Am. Chem. Soc. **126**, 1235 (2004).
[11] J. M. Michaud, S. A. Cooke, and M. C. L. Gerry, Inorg. Chem. **43**, 3871 (2004).
[12] J. M. Michaud and M. C. L. Gerry, J. Am. Chem. Soc. **128**, 7613 (2006).
[13] T. K. Ghanty, J. Chem. Phys. **123**, 074323 (2005).
[14] T. K. Ghanty, J. Chem. Phys. **124**, 124304 (2006).
[15] J. M. Michaud and M. C. L. Gerry, J. Am. Chem. Soc. **128**, 7613 (2006).
[16] S. Seidel and K. Seppelt, Science **290**, 117 (2000).
[17] P. Pyykkö, J. Am. Chem. Soc. **117**, 2067 (1995).
[18] L. Belpassi, I. Infante, F. Tarantelli, and L. Visscher, J. Am. Chem. Soc. (in print).
[19] A. Nicklass, M. Dolg, H. Stoll, and H. Preuss, J. Chem. Phys. **102**, 8942 (1995).
[20] D. Schröder, J. N. Harvey, M. Aschi, and H. Schwarz, J. Chem. Phys. **108**, 8446 (1998).
[21] G. Chalasiński and M. M. Szczęśnial, Chem. Rev. **94**, 1723 (1994).
[22] L. Xinying *et al.*, J. Mol. Struct. (THEOCHEM) **755**, 215 (2005); X. Li *et al.*, Int. J. Quantum Chem. **106**, 1086 (2006); L. Xinying *et al.*, Phys. Scr. **73**, 103 (2006); X. Li *et al.*, Chem. Phys. **328**, 64 (2006).
[23] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, Theor. Chim. Acta **77**, 123 (1990).
[24] M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. **86**, 866 (1987).
[25] P. Pyykkö, N. Runeberg, and F. Mendizabal, Chem. Eur. J. **3**, 1451 (1997).
[26] D. Schröder, S. H. Schwarz, J. Hrusÿak, and P. Pyykkö, Inorg.

Chem. **37**, 624 (1998).
[27] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).
[28] M. J. Frisch *et al.*, GAUSSIAN 03 W, Gaussian, Inc., Pittsburgh, PA, 1998.
[29] R. J. Bartlett and G. D. Purvis III, Ann. N. Y. Acad. Sci. **367**, 62 (1981).
[30] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).
[31] N. Oliphant and R. J. Barlett, J. Chem. Phys. **100**, 6550 (1994).
[32] G. Fitzgerald, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **85**, 1701 (1986).
[33] D. Schröder, H. Schwarz, J. Hrusak, and P. Pyykkö, Inorg. Chem. **37**, 624 (1998).
[34] E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. A **49**, 1724 (1994).
[35] P. Schwerdtfeger, Chem. Phys. Lett. **183**, 457 (1991).