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Studies of Neutral and Ionic CuAr and CuKr van der Waals Complexes

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Ab initio calculations of the interaction potential between Cu (or Cu^+) and Ar (or Kr) have been carried out. A range of theoretical methods, including Hartree−Fock (HF), Moeller−Plesset perturbation methods to second order (MP2), and single and double excitation coupled cluster methods, with the perturbational effect of triple excitations (CCSD(T)), were employed with relativistic pseudopotential basis sets. The effects of bond functions and diffuse polarization (f, g, h) functions were tested on the calculation of the weak intermolecular interactions. Potential energy curves were obtained for all four complexes by MP2 and CCSD(T) methods. For CuKr, even with the largest basis set used, a binding energy that is only 37% of the measured value was obtained. Possible reasons for the disagreement are discussed.

1. Introduction

There have been a large number of spectroscopic and theoretical studies of the interaction of metal atoms or ions with rare gas atoms.[1−4] Interactions between metal atoms and rare gas matrixes are common. These interactions can be significant and lead to the well-known matrix effect: a shift in the spectral features relative to the uncomplexed species. Studies of the interactions in simple systems composed of one metal atom, M, and one or more rare-gas atoms, Rg, can provide insight into the interatomic potentials. A case in point is the reported frequency shifts of the transition metal atoms, Ru, Os, Ir, Ni, Mo, Ag, and Au in argon, krypton, and xenon matrixes.[5] A modified Lennard-Jones (6-12) potential was successfully used to investigate the relationship between the matrix induced frequency shifts and the rare gas polarizabilities. The studies of metal ion−rare gas atom interactions are also important for understanding the electrostatic interaction of metal ions, which are ubiquitous in chemistry and biochemistry. For example, ionic interactions affect the binding on many catalytic, metal oxide surfaces[6] and the electrostatic interactions of metal ions at the active sites of many enzymes influence binding. The simplest electrostatic complexes, diatomic molecules formed from a single rare-gas atom bound to a metal cation, are ideal for investigating such fundamental electrostatic interactions, as they have easily described electronic states.[7] In this paper, we are interested in studies of simple systems composed of a single copper atom or cation with one argon or krypton atom. It is a preliminary step in the theoretical investigation, based on density functional theory (DFT) methods, of the photodissociation spectra of Cu_3Ar and Cu_3Kr, which have anomalously large blue shifts of ∼700 cm^{-1} with respect to the Cu_3 $\tilde{A} \leftarrow \tilde{X}$ origin.[8]

It is generally accepted that interactions in simple systems composed of one metal atom and one or more rare-gas atoms can serve as model systems for the investigation of chemical reactions involving the same metal atom and small molecules. The results from a series of ab initio calculations on CuAr/CuKr may serve as comparison data for the performance of different functionals for such systems, because different density functionals have different performances for weakly interacting systems. For example, DFT methods based on Becke-type functionals[9,10] yield repulsive interactions for noble gas dimers,[11,12] whereas DFT methods based on the Perdew-type functionals[13] predict interaction energies for He_2 and Ne_2 that are several times too large.[14,15] The ab initio calculations also have intrinsic value, because little experimental information is available concerning these systems. The photoionization spectroscopy of CuKr was reported by Brock and Duncan.[16] They obtained a dissociation energy of 408 cm^{-1} for the ground $^2\Sigma_{1/2}$ state and dissociation energies of 1842 and 2009 cm^{-1} for the excited $^2\Pi_{1/2,3/2}$ states. However, no spectrum was obtained for Cu^+-Kr, CuAr, or Cu^+Ar in the gas phase. The only calculation for Cu^+Kr was done by Bauschlicher et al.[17a] using a modified coupled-pair functional (MCPF). For Cu^+Ar, values of D_0 were reported by Hammond and Lester[17b] with UHF and CISDQ methods and by Partridge et al.[17c] with the MCPF method. High-level theoretical calculations are also required for these simple vdW systems to predict gas-phase spectra.

In this paper, we focus on ab initio calculations of the interaction potential between Cu/Cu^+ and Ar/Kr. The theoretical methods used include HF, MP2, and CCSD(T). Because the methods include different levels of electron correlation, comparison of the results from these methods can assess the importance of electron correlation in the metal−rare gas interactions.

2. Computational Methods

2.1. Basis Set Effects on Ionization Energy, Electron Affinity, and Polarizability. The calculations were performed using *NWChem 4.6*.[18] Because the bonding of noble gas atoms in these molecules is mainly due to dispersion effects, one needs to use basis sets that are capable of reproducing the atomic polarizabilities. Thus, the 19-valence electron, quasi-relativistic pseudopotential developed by Dolg et al.[19] was used for copper. For Ar and Kr, the 8-valence electron relativistic energy-adjusted pseudopotentials of Nicklass et al.[20] were used.

It has been shown that f orbitals are important for a correct description of weak intermolecular interactions involving transition metal atoms.[21,22] The effect on the CCSD(T) ionization energies and electron affinities of adding these functions is shown in Table 1 for the copper atom, initially using two f-type polarization functions optimized for the ground-state energy by the same theoretical method. The optimized exponents in these

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TABLE 1: CCSD(T) Ionization Energy (IE) and Electron Affinity (EA) of the Copper Atom

	f exponents				
	none	5.27; 1.36	5.27; 1.36; 0.453	1.36; 0.453	exp
IE (eV)	7.269	7.498	7.675	7.673	7.735[23]
EA (eV)	1.084	1.119	1.180	1.184	1.226[24]

functions were 1.36 and 5.27. However, we need to also examine the excited states of molecules containing the copper atom and a diffuse function might play an important role in the excitation energy. Therefore, we also calculated the atomic properties using a third polarization function with an exponent of 0.453, as well as using combinations of these diffuse and contracted functions. As is clear from Table 1, without the f-type functions, the calculated copper ionization energy, IE, 7.269 eV, is significantly smaller than the experimental value of 7.735 eV and the calculated electron affinity, EA, is 0.14 eV less than the experimental value. The addition of the two f-type functions optimized for the total ground-state energy improved the results, but the calculated values remained smaller than those determined experimentally. Addition of the third polarization function, $\alpha_f = 0.453$, led to calculated values of IE and EA in much better agreement with the experimental values. The relative errors are ~1% and ~5%, respectively for the IE and EA. Removing the most contracted f-type function and retaining only the more diffuse functions, resulted in calculated parameters that are essentially identical to those from the three f-type function calculation; the effect of the most contracted function is negligible. Thus, we initially retained only the more diffuse f-type functions for our later calculations. The initial basis sets are then the 19-valence electron (8s7p6d2f)/[6s5p3d2f] Gaussian basis set for Cu and the 8-valence electron (6s6p3d1f)/[4s4p3d1f] for Ar/Kr. It is critical that the basis set used in the potential calculations be sufficiently large so as to accurately describe the interaction. To this end, additional basis sets were constructed.

We further augmented the argon and krypton valence basis sets with one diffuse s, p, and f function having the exponential parameters (0.044; 0.032; 0.311) and (0.057; 0.036; 0.240), respectively, and added a single diffuse f function with the exponential parameter 0.15 to the copper valence electron basis set. The result was the second, slightly larger (7s7p3d2f)/[5s5p3d2f] Gaussian basis set for Ar/Kr and (8s7p6d3f)/[6s5p3d3f] Gaussian basis set for copper.

Additional augmentation of the basis set was achieved by stepwise addition of an increasing number of f, g, and h polarization functions to the (7s7p3d2f)/[5s5p3d2f] and (8s7p6d3f)/[6s5p3d3f] basis sets. The largest atomic basis sets developed and used in the calculations resulted from this operation and are the (7s7p3d3f3g3h)/[5s5p3d3f3g3h] Gaussian atomic basis set for Ar/Kr and the (8s7p6d4f3g3h)/[6s5p3d4f3g3h] Gaussian atomic basis set for Cu, where one f, three g, and three h functions were added to the (7s7p3d2f)/[5s5p3d2f] atomic basis set for Ar/Kr and to the (8s7p6d3f)/[6s5p3d3f] atomic basis set for Cu. The exponents for the added diffuse polarization functions are listed in Table 2. The calculated ionization energies and polarizabilities, obtained from finite-field calculations with a field strength of 0.001 au by the HF, MP2, and CCSD(T) theoretical methods with the (7s7p3d2f)/[5s5p3d2f] Gaussian basis set for Ar/Kr, and the (8s7p6d3f)/[6s5p3d3f] Gaussian basis set for Cu are shown in Table 3. The Hartree−Fock ionization energies are consistently too low for all three elements; the errors are greater than 1 eV. The addition of correlation effects via the MP2 method improved the results for all three atoms; errors, when compared with the experimental values, were less than 0.18 eV. The CCSD(T) method resulted in ionization energies somewhat smaller than those from the MP2 method; however, errors were less than 0.26 eV.

TABLE 2: Exponents for the s, p, f, g, and h Functions Added to the Initial (8s7p6d2f)/[6s5p3d2f] Gaussian Basis Set for Cu and the 8-Valence Electron (6s6p3d1f)/[4s4p3d1f] for Ar/Kr

additional functions	exponent (Cu)	exponent (Ar/Kr)
s		0.044/0.057
p		0.032/0.036
f	0.15	0.311/0.240
2f	0.15, 0.05	0.311, 0.104/0.240, 0.080
g	1.00	1.00
2g	1.00, 0.33	1.00, 0.33
3g	1.00, 0.33, 0.11	1.00, 0.33, 0.11
h	1.00	1.00
2h	1.00, 0.33	1.00, 0.33
3h	1.00, 0.33, 0.11	1.00, 0.33, 0.11

TABLE 3: Ionization Energies and Polarizabilities for Copper, Argon, and Krypton Atoms Calculated at Different Levels of Theory Using the (7s7p3d2f)/[5s5p3d2f] Gaussian Basis Set for Ar/Kr and the (8s7p6d3f)/[6s5p3d3f] Gaussian Basis Set for Cu (Initial Basis Set Results in Parentheses)

properties/method	Cu	Ar	Kr
IE, eV			
HF	6.656 (6.656)	14.541 (14.548)	13.060 (13.070)
MP2	7.728 (7.716)	15.727 (15.688)	14.047 (14.012)
CCSD(T)	7.697 (7.673)	15.584 (15.543)	13.963 (13.928)
expt[23]	7.735	15.819	14.222
α, a_0^3			
HF	67.349 (67.147)	10.538 (10.297)	15.974 (14.152)
MP2	34.780 (34.616)	10.949 (10.499)	16.493 (14.161)
CCSD(T)	46.326 (46.232)	10.974 (10.523)	16.603 (14.207)
expt	45.214[25]	11.08,[26] 11.221[27]	16.79,[26] 17.075[27]

For polarizabilities, the HF method yielded extremely poor results for copper, with an error of 22.135 a_0^3. The results for argon and krypton also have significant error. The use of the MP2 method dramatically improved the results for all three atoms. However, the result for copper remained smaller than the experimental value by 10.434 a_0^3. Finally, the CCSD(T) method decreased the relative errors to less than 2.5%. Overall, the CCSD(T) method provided the best results for ionization energy and polarizability considered simultaneously. The effect on the ionization energies and dipole polarizabilities of adding diffuse s, p, and f functions to the Ar/Kr basis sets and a diffuse f function to that for copper were obvious when parameters calculated from the initial basis sets (Table 3 values in parentheses) are compared with the values from the augmented basis set. The change in the ionization energies is slight, with an increase smaller than 0.04 eV in all three atoms. The effect on the polarizability of copper is also small. However, the polarizabilities of argon and krypton are very much improved; the relative error for the CCSD(T) results were approximately 1% with the augmented basis set. The use of additional f, g, and h polarization functions in the basis sets was not studied in the ionization energy/polarization calculations but would be expected to provide results at least equivalent to those noted here.

Because bond functions supplementing atomic basis sets have proven highly effective in offsetting major deficiencies in ab initio calculations of intermolecular potentials, especially for weakly bound systems,[28] we included the fixed set of bond functions, {3s3p2d}, with s and p exponents 0.9, 0.3, and 0.1, and d exponents 0.6 and 0.2, put forward by Tao and Pan[29] in their He_2 study. These functions were located at the geometric center of the vdW complexes in the interatomic potential

TABLE 4: Calculated Binding Energy (eV) with BSSE Correction for CuKr at $R = 3.9$ Å Using Several Atomic Basis Sets and Bond Functions

		no bond function			{3s3p2d}			{3s3p2dfg}		
Cu basis set	Kr basis set	V^{MP2}	V^{HF}	V^{CORR}	V^{MP2}	V^{HF}	V^{CORR}	V^{MP2}	V^{HF}	V^{CORR}
8s7p6d2f/[6s5p3d2f]	6s6p3d1f/[4s4p3d1f]	−0.0095	0.0386	−0.0481	−0.0191	0.0383	−0.0574	−0.0199	0.0386	−0.0585
8s7p6d3f/[6s5p3d3f]	7s7p3d2f/[5s5p3d2f]	−0.0157	0.0383	−0.0540	−0.0202	0.0382	−0.0584	−0.0209	0.0384	−0.0593
8s7p6d3f1g/[6s5p3d3f1g]	7s7p3d2f/[5s5p3d2f1g]	−0.0164	0.0383	−0.0547	−0.0209	0.0382	−0.0591	−0.0214	0.0384	−0.0598
8s7p6d3f2g/[6s5p3d3f2g]	7s7p3d2f2g/[5s5p3d2f2g]	−0.0183	0.0383	−0.0566	−0.0215	0.0382	−0.0597	−0.0217	0.0384	−0.0601
8s7p6d3f2g1h/[6s5p3d3f2g1h]	7s7p3d2f2g1h/[5s5p3d2f2g1h]	−0.0186	0.0383	−0.0569	−0.0217	0.0382	−0.0599	−0.0219	0.0384	−0.0603
8s7p6d3f2g2h/[6s5p3d3f2g2h]	7s7p3d2f2g2h/[5s5p3d2f2g2h]	−0.0193	0.0383	−0.0576	−0.0219	0.0382	−0.0601	−0.0221	0.0384	−0.0605
8s7p6d4f3g3h/[6s5p3d4f3g3h]	7s7p3d3f3g3h/[5s5p3d3f3g3h]	−0.0205	0.0383	−0.0588	−0.0226	0.0382	−0.0608	−0.0226	0.0383	−0.0609

calculations. This particular set of bond functions has been verified by many researchers in studies of different systems[30,31] to be well balanced and effective over a wide range of intermolecular distances. Finally, an augmented set of bond functions, which was derived by adding one f and one g function suggested by Duijneveldt et al.[32] with exponents 0.40 and 0.60, respectively, to the {3s3p2d} set of bond functions was also tested in the calculations for CuKr.

2.2. Basis Set Superposition Error (BSSE). A calculation of the interaction energy of two fragments requires the energy difference between the supermolecule and the energy of the separated fragments. In the case of weak interactions, special care must be taken with the calculation. The fragment calculations must address the problem posed by the basis set superposition error (BSSE), widely recognized as the bane of weak interaction calculations. Despite the fact that extended basis sets were used in our calculations, the BSSE values were not negligible. Thus, a counterpoise correction for the BSSE[33] was performed, according to

$$\Delta E(\mathrm{BSSE,A{-}B}) = E(\mathrm{A})_{\mathrm{A}} - E(\mathrm{A})_{\mathrm{A-B}} + E(\mathrm{B})_{\mathrm{B}} - E(\mathrm{B})_{\mathrm{A-B}} \tag{1}$$

where $E(\mathrm{A})_{\mathrm{A-B}}$ and $E(\mathrm{A})_{\mathrm{A}}$ are the energies of fragment A calculated using its geometry within the dimer and the full dimer basis set in $E(\mathrm{A})_{\mathrm{A-B}}$ and those of A alone in $E(\mathrm{A})_{\mathrm{A}}$. Accordingly, the interaction energy, V, as a function of the internuclear distance, R, between A and B is obtained from

$$V(\mathrm{R}) = E(\mathrm{AB})_{\mathrm{A-B}} - E(\mathrm{A})_{\mathrm{A-B}} - E(\mathrm{B})_{\mathrm{A-B}} \tag{2}$$

The magnitude of the BSSE correction is approximately equal to the binding energy near the equilibrium interatomic distance for the neutral complexes. For the smallest and the largest basis sets and the CCSD(T) theoretical method, the values of ΔE(BSSE,A−B) are 0.016 and 0.030 eV, respectively. For the cationic species, the corresponding values are 0.09 and 0.15 eV.

2.3. Theoretical Methods: Effect on the Potential Energy. The first step in the determination of the potential energy for the vdW molecules is to confirm the suitability of the atomic basis set/bond functions by calculating the binding energy for CuKr at the HF and MP2 levels of theory, using an interatomic separation of 3.9 Å. As CuAr and CuKr are similar, the results from this test would be equally valid for CuAr. The calculated binding energies after the BSSE correction, using different combinations of atomic basis sets/bond functions, are reported in Table 4. The correlation contributions at the MP2 level of theory are calculated by

$$V(\mathrm{R}) = V^{\mathrm{SCF}} + V^{\mathrm{CORR}} \tag{3}$$

and are also provided in the table. For all of the calculations, we used the contracted basis sets to reduce the computational effort. The BSSE-corrected binding energies are nearly identical when the basis sets with the contraction and without the contraction are used, as confirmed by our own testing and the results from Murno and Johnson.[34]

As is clear from Table 4, V^{HF} converges rapidly with increasing complexity of the basis set and is repulsive at $R = 3.9$ Å; the attractive contribution in V^{MP2} comes exclusively from V^{CORR}. This indicates the critical importance of an accurate treatment of electron correlation in recovering the well depth and the attractive region of the intermolecular potential. The correlation contribution, V^{CORR}, converges much more slowly with basis set as it primarily recovers the dispersion energy. With the addition of bond functions, either the {3s3p2d} or {3s3p2dfg} set, the convergence of V^{MP2} is dramatically and systematically improved. The use of either bond function set also increases V^{MP2} by approximately 0.002 eV at this distance for the largest atomic basis set. One usual concern about the use of bond functions is distortion in the molecular electronic distribution, which can be reflected by changes in V^{HF}. If there is no severe distortion in the molecular electronic distribution, then the changes in V^{HF} should be rather small, because the bond functions were primarily intended to recover the correlation contribution, V^{CORR}. From the table, we see that the changes in V^{HF} by the addition of either bond function set are extremely small, less than 0.0003 eV in all cases. Thus, we are confident in the suitability of the bond functions used in our calculation, as well as the adequacy of the atomic basis sets used in the description of the core and valence electron wave functions. Comparing the calculated results between the two bond function sets, it is obvious that the differences between them are negligible, the largest difference is 0.0008 eV and decreases systematically with the increase in the size of the atomic basis sets. For the largest atomic basis set, there is essentially no difference in the results. Thus, for our calculations, we used the {3s3p2d} set to reduce the computational effort.

To include high-level electron correlation effects via the CCSD(T) theoretical method, which is computationally demanding when using large basis sets, we followed the methodology presented by Murno and Johnson.[34] in their calculations of the interatomic potential for the mercury dimer. They implemented a G2-type approach to include electron correlation effects via the following formula:

$$E^{\mathrm{Large}}_{\mathrm{CCSD(T)est}} = E^{\mathrm{Small}}_{\mathrm{CCSD(T)}} + E^{\mathrm{Large}}_{\mathrm{MP2}} - E^{\mathrm{Small}}_{\mathrm{MP2}} \tag{4}$$

Here, $E^{\mathrm{Small}}_{\mathrm{CCSD(T)}}$ is the CCSD(T) interaction energy calculated using a small basis set and contributions from additional higher angular momentum functions are estimated by the difference in an MP2 calculation involving the same small basis set and a larger basis set. To assess the importance of electron correlation in the intermolecular interactions, one may, to a good approximation,[35] partition the total interaction potential as shown in eq 3, where V^{SCF} is the sum of V^{short}, V^{elect}, and V^{ind}, the

TABLE 5: Calculated and Estimated Binding Energies for Cu/Kr in cm^{-1} at R = 3.9 Å, Using Different Atomic Basis Sets, with the {3s3p2d} Bond Function Set

large basis sets	small basis sets	$V^{\mathrm{calc}}_{\mathrm{CCSD(T)}}$	$V^{\mathrm{est}}_{\mathrm{CCSD(T)}}$	error	%error
6s5p3d2f/4s4p3d1f		−118.8			
6s5p3d3f/5s5p3d2f (A)	6s5p3d2f/4s4p3d1f	−129.6	−127.5	2.1	+1.6
6s5p3d3f2g/5s5p3d2f2g (B)	6s5p3d2f/4s4p3d1f	−140.0	−137.6	2.4	+1.7
	6s5p3d3f/5s5p3d2f		−139.6	0.4	+0.3
6s5p3d3f2g2h/5s5p3d2f2g2h (C)	6s5p3d2f/4s4p3d1f	−143.8	−141.1	2.7	+1.9
	6s5p3d3f/5s5p3d2f		−143.2	0.6	+0.4
	6s5p3d3f2g/5s5p3d2f2g		−143.4	0.4	+0.3
6s5p3d4f3g3h/5s5p3d3f3g3h (D)	6s5p3d2f/4s4p3d1f		−146.8	3.1[a]	+2.1[a]
	6s5p3d3f/5s5p3d2f		−148.9	1.0[a]	+0.7[a]
	6s5p3d3f2g/5s5p3d2f2g		−149.9		

[a] Calculated using the value of −149.9 cm^{-1} estimated using the 6s5p3d3f2g/5s5p3d2f2g basis set combination, due to the lack of an exact calculated CCSD(T) binding energy.

short-range, electrostatic, and induction contributions, respectively. V^{CORR}, as noted above, is approximately the dispersion energy. It is the dominant attractive force between nonpolar molecules. To implement the G2-type approach, one must calculate binding energies, using both the MP2 and CCSD(T) methods, at the internuclear separation of 3.9 Å. As shown in Table 4, the increase in binding energies for the addition of a single g or h function is small, so we only consider for choice of basis set, those in rows 1, 2, 4, 6, and 7 in Table 4. The calculated and estimated CCSD(T) interaction energy from eq 4, the absolute error and the relative error are listed in Table 5 for CuKr. It is clear from the relative error that both the 6s5p3d2f/4s4p3d1f + {3s3p2d} and the 6s5p3d3f/5s5p3d2f + {3s3p2d} basis sets are excellent choices for the small basis set. The relative error in estimating the larger basis set CCSD(T) binding energies from these basis sets is smaller than 2.1%. However, the 6s5p3d3f/5s5p3d2f + {3s3p2d} basis set provides somewhat superior results. Thus, this basis set will be used as the small basis set for calculations of the CuKr potential. The corresponding 6s5p3d3f/5s5p3d2f + {3s3p2d} basis set will be used for CuAr.

3. Results and Discussions

3.1. CuKr/CuAr. CuKr potential energy curves calculated at the CCSD(T) level of theory with the large basis sets (row 2 in Table 5) and those estimated by means of eq 4 with the large basis sets (in rows 3, 5 and 8) are presented in Figure 1a. Corresponding basis sets were used for CuAr calculations and the curves are presented in Figure 1b. These curves were produced using a standard cubic spline interpolation between calculated energy points. The BSSE corrections were made on a point-by-point basis along the potential curves. Equilibrium interactomic distances, R_e, and well depths, D_0, for CuKr/Ar were obtained by fitting the six lowest-energy points of the corresponding potential curves to a fifth-order polynomial in R. The results are displayed in Table 6. The resultant D_e values were compared with the energies, D_e^{cal}, calculated at the derived value of R_e (also listed in Table 6). For all cases studied, excellent agreement was found; the variation was always less than 2 cm^{-1}. This suggests that the errors arising from interpolation and/or the G2-type approach are rather small.

As is clear from Table 6, the inclusion of g and h functions shortens R_e and increases D_e, for both CuKr and CuAr. The shortening in R_e by adding two g and h functions is 0.05 Å for CuKr and 0.11 Å for CuAr, whereas the increases in D_e are 10.4% and 18.8%. Further addition of f, g, and h functions reduces R_e by 0.01 Å for CuKr and 0.06 Å for CuAr. The largest basis set in Table 6 results in a value of D_e that is 1.15 times that from the smallest basis set for CuKr, with a corresponding value of 1.32 for CuAr. However, the CuKr binding energy calculated using the largest basis set, 149.3 cm^{-1}, is only 37% of the experimental binding energy of 408 cm^{-1}. One must

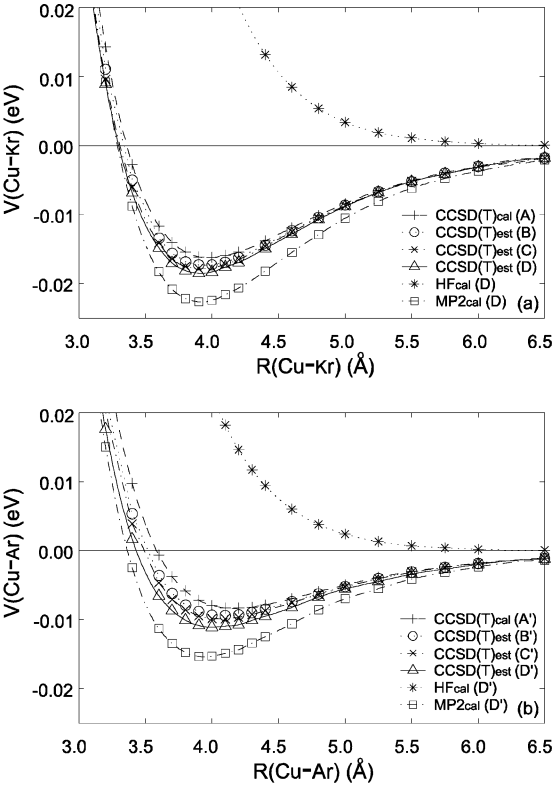

Figure 1. Potential energy curves calculated or estimated at the CCSD(T) levels of theory with different basis sets, A−D (or Ar equivalent), in Table 5 for (a) CuKr and (b) CuAr. The calculated HF and MP2 curves for basis set D are also displayed.

TABLE 6: Optimized CuAr and CuKr Distances and Dissociation Energies with the BSSE Correction, Using Different Basis Sets

molecule	method	basis set	R_e, Å	D_e, cm^{-1}	D_e^{cal}, cm^{-1}
CuKr	CCSD(T)	A	3.98	130.8	130.9
	CCSD(T)	B	3.94	140.0	141.1
	CCSD(T)	C	3.93	143.3	144.5
	CCSD(T)	D	3.92	149.3	
	MP2	D	3.92	182.5	182.5
	Expt			408[16]	
CuAr	CCSD(T)	A′	4.17	67.4	67.6
	CCSD(T)	B′	4.08	76.2	77.4
	CCSD(T)	C′	4.06	79.7	80.3
	CCSD(T)	D′	4.00	89.3	
	MP2	D′	3.94	124.0	124.0

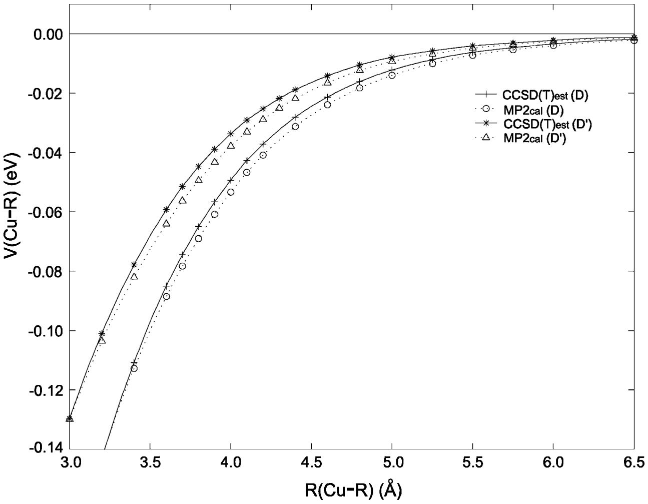

Figure 2. Correlation energy at CCSD(T) and MP2 level with basis set D along the *R* coordinate for (a) CuAr and (b) CuKr.

explore the possible reasons for the large difference between the calculated and the experimental binding energies.

In their report on the photoionization spectroscopy of CuKr, Brock and Duncan[16] observed an interesting trend when they compared the binding energies of the CuKr ground state with that for AgKr. The ground-state dissociation energy for CuKr, 408 cm^{-1}, was approximately 3 times greater than that for AgKr, 138 cm^{-1}. This was a surprising result because the polarizability of silver is greater than that of copper. Therefore one would expect AgKr to have the larger dissociation energy. The authors[16] argued that the observation was due to the different extent of hybridization in the CuKr and AgKr complexes arising from interactions between the $^2\Sigma$ ground state and the $^2\Delta$ excited state. In copper, the ^{2}S ground state and the ^{2}D excited state, separated by approximately 13 000 cm^{-1}, interact strongly in the CuKr complex. This leads to efficient sd hybridization, reducing the repulsion and/or increasing the attraction between the two atoms, and resulting in a greater binding energy in the CuKr $^2\Sigma$ ground state. However, the ^{2}S ground state and the ^{2}D excited state are separated by approximately 30 000 cm^{-1} in Ag. Thus, sd hybridization is much less efficient. Assuming this argument is correct, one must take into account the contribution of interaction between the ^{2}S and ^{2}D states in the theoretical calculations of the binding energy. Single reference methods, such as CCSD(T), might not be able to handle the interaction effectively. Miyoshi[36] observed that it is important to consider the reorganization effect when the d electron is excited in Cu. Thus, the final CCSD(T) wave function, though optimized for the $^2\Sigma$ ground state, might be a poor description of the $^2\Delta$ excited state. To take into account the full reorganization effect, one might use the multireference configuration interaction (MRCI) method. However, a MRCI calculation is beyond the scope of this paper.

At the Hartree−Fock level of theory, the interaction energies are everywhere repulsive for both vdW molecules; only after inclusion of electron correlation does an attractive portion of the potential appear. To examine the correlation energy contribution at different values of *R*, we plot the correlation energy for CCSD(T)$_{\rm est}$ and MP2$_{\rm cal}$ (with basis set D), calculated by eq 3, along the *R* coordinate in Figure 2 for CuAr and CuKr. As expected, the correlation interaction is always attractive. From Figure 2, we observe that the MP2 correlation energy is somewhat larger in magnitude than that from CCSD(T), as is usually observed in the calculations of vdW interactions. This trend is also obvious in Figure 1, where the MP2$_{\rm cal}$ (basis set D) curves are more attractive than the CCSD(T)$_{\rm est}$ curves for both vdW complexes.

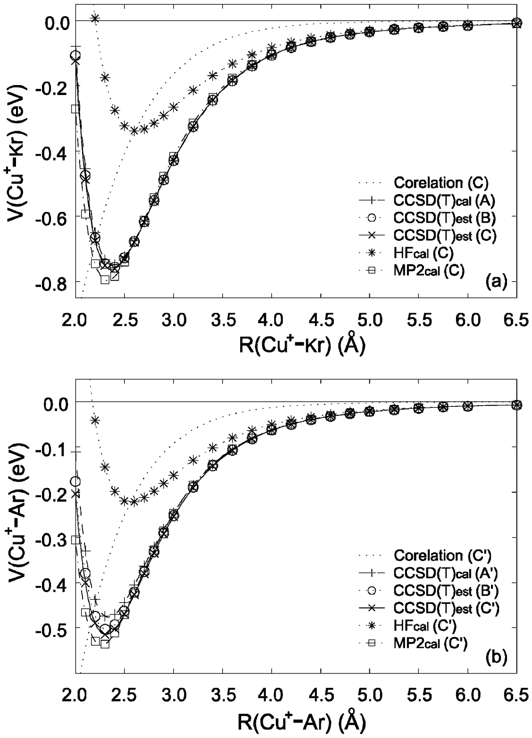

Figure 3. Potential energy curves calculated or estimated at the CCSD(T) levels of theory with different basis sets different basis sets, A−D (or Ar equivalent), in Table 5 for (a) Cu$^+$Kr and (b) Cu$^+$Ar. The calculated HF and MP2 curves and correlation energy contributions for the CCSD(T) (basis set C or Ar equivalent) curves are also displayed.

Table 6 indicates that the largest value of D_e for CuKr from CCSD(T) calculations is 149.3 cm^{-1}, and that for CuAr is 89.3 cm^{-1}. The ratio of these two results is 1.67. If we consider the dipole contribution and ignore higher-order multipole terms in the dispersion energy, the London approximation[37] for the calculation of dispersion energy for CuAr/Kr is given by

$$V^{\rm disp} = -\frac{C}{R^6} = \alpha\frac{3{\rm IE}_1^{\rm Cu}\,{\rm IE}_1^{\rm Rg}\alpha^{\rm Cu}\alpha^{\rm Rg}}{2({\rm IE}_1{}^{\rm Cu} + {\rm IE}_1{}^{\rm Rg})R^6} \qquad (5)$$

where ${\rm IE}_1^{\rm Cu}$ and ${\rm IE}_1^{\rm Rg}$ are the first ionization energies and $\alpha^{\rm Cu}$ and $\alpha^{\rm Rg}$ are the static polarizabilities for Cu and Ar/Kr, respectively. Equation 5 provides a classical explanation for the fact that CuKr has a larger binding energy than CuAr. If we use the CCSD(T) IE$_1$ and α values from Table 2, and the CCSD(T) (basis set D) R_e values from Table 6, eq 5 predicts the dispersion energy of CuKr to be 1.65 times that of CuAr. This ratio of 1.65 has a major contribution from $\alpha^{\rm Kr}/\alpha^{\rm Ar}$, which is 1.52. Thus, within the current model, CuKr has a larger binding energy than CuAr at the minimum, because the krypton atom is more polarizable than the argon atom. The difference in the polarizability also results in a slightly different equilibrium separation, R_e, with that for CuKr, 3.92 Å, being 0.08 Å smaller than that for CuAr, 4.00 Å. The trend in dispersion energy is also obvious in Figure 2, which shows that the correlation energy for CuKr is always more attractive than that for CuAr.

3.2. Cu$^+$Ar/Cu$^+$Kr. Potential energy curves calculated using basis set C at the HF, MP2, and CCSD(T) levels of theory for the ground states of Cu$^+$Kr and Cu$^+$Ar ($^1\Sigma^+$:(Cu $3d^{10}$)), are presented in Figure 3a,b, respectively. As in the neutral case,

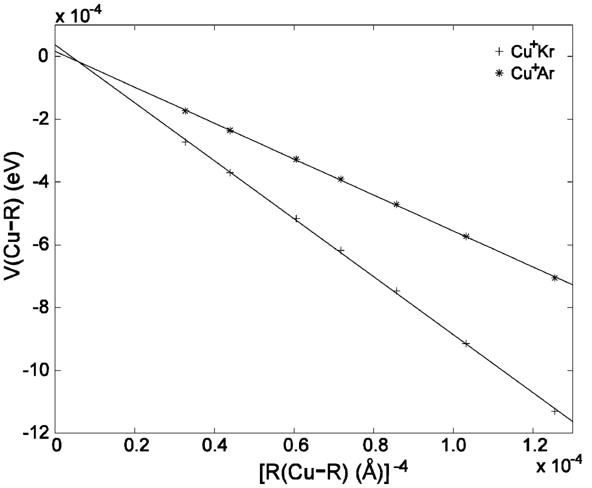

Figure 4. Linear fitting of the HF interaction energy as a function of R^{-4} ($R \geq 5.0$ Å), for CuKr and CuAr.

TABLE 7: Optimized Cu$^+$Ar and Cu$^+$Kr Distances and Dissociation Energies with the BSSE Correction, at Different Levels of Theory

molecule	method	basis set	R_e, Å	D_e, eV	D_e^{cal}, eV
Cu$^+$Kr	CCSD(T)	A	2.38	0.749	0.749
	CCSD(T)	B	2.37	0.758	0.758
	CCSD(T)	C	2.37	0.762	0.762
	HF	C	2.61	0.338	0.338
	MP2	C	2.32	0.796	0.796
	MCPF[17(a)]		2.46	0.581	
Cu$^+$Ar	CCSD(T)	A′	2.34	0.477	0.477
	CCSD(T)	B′	2.32	0.504	0.504
	CCSD(T)	C′	2.31	0.515	0.515
	HF	C′	2.56	0.222	0.222
	MP2	C′	2.26	0.539	0.539
	HF[17(b)]		2.62	0.194	
	CISDQ[17(b)]		2.51	0.460	
	MCPF[17(c)]		2.37	0.405	

the MP2 curves are more attractive than the CCSD(T) curves for both vdW complexes. The calculated and estimated CCSD(T) potential curves for basis sets A and B are also plotted for comparison purposes, as are the correlation energy contributions for the CCSD(T) (basis C) curves. Contrary to the neutral systems, energy wells appeared even at the Hartree−Fock level of theory, indicating that the exchange interaction plays a role in these systems, though the exchange interaction alone cannot be sufficient to describe the interaction. The HF interaction is repulsive at $R \leq 2.2$ Å and attractive at larger distances. For the CCSD(T) potential, the exchange and the correlation energies contribute to a similar extent near $R = 2.6$ Å for both Cu$^+$Ar and Cu$^+$Kr. Prior to that distance, the exchange interaction contributes less to the attractive potential than does the correlation interaction. The relative contributions of these two terms are opposite in magnitude beyond $R = 2.6$ Å. When $R \geq 4.5$ Å, binding arises almost exclusively from the exchange interaction, evidenced by the fact that the HF curve overlaps that from the CCSD(T) calculation. At long range, where there is no charge overlap between the electron clouds of Cu$^+$ and Ar/Kr, V^{short}, the valence repulsion term that arises from interatomic Coulomb and exchange terms involving electrons on different monomers, vanishes. At this point, the electrostatic and induction terms are classical. Because the formal charge for argon and krypton is zero, the long-range electrostatic energy also vanishes. The Cu$^+$Ar/ Cu$^+$Kr molecule can be viewed as an unperturbed Cu$^+$ ion bound to Ar or Kr by simple charge-induced dipole forces. The classical form of interaction between Cu$^+$ and the Ar or Kr electron cloud is given by

$$V^{ind} = \alpha\frac{1}{2}\frac{\alpha q^2}{R^4} \tag{6}$$

where Cu$^+$ is treated as a point charge with $q = 1$ and α is the polarizability of argon or krypton. Linear fitting of the HF interaction energy as a function of R^{-4}, when $R \geq 5.0$ Å, yields the two lines in Figure 4. Ignoring the least-squares residues, which are extremely small and result from a combination of all the approximations and numerical errors in the computation and linear-fitting processes, the slopes of the two lines yield the polarizabilities of the rare gas atoms: 11.448 a_0^3 for argon and 17.451 a_0^3 for krypton. These values are in excellent agreement with the experimental values[27] of 11.221 a_0^3 for argon and 17.075 a_0^3 for krypton. This indicates that eq 6 is a good approximation to the HF interaction energy of Cu$^+$Kr/Ar when $R \geq 5.0$ Å.

The optimized Cu$^+$Ar/ Cu$^+$Kr distances and binding energies at HF (basis set C), MP2 (basis set C), and CCSD(T) (basis sets A−C) levels of calculation, are displayed in Table 7. From the table, one may observe that the inclusion of g and h functions again decreases the optimized Cu$^+$Ar/Cu$^+$Kr distances and increases the binding energies, but the effects are much less pronounced than those observed for the neutral molecules. The decreases in R_e are 0.01 and 0.03 Å and the relative increases in the binding energies are 1.7% and 7.4% from basis set A to basis set C for Cu$^+$Kr and Cu$^+$Ar, respectively.

For all of the methods, the value of R_e for Cu$^+$Kr is 0.04−0.06 Å longer than the value for Cu$^+$Ar and the D_e results for Cu$^+$Kr are greater than those for the argon analogue. This observation reflects the fact that the interaction is mainly due to charge-induced dipole forces and the larger atomic polarizability of krypton will result in a larger induced dipole and, subsequently, a larger D_e. On the other hand, the krypton atom has a larger radius (0.88 Å) than the argon atom (0.71 Å), so that R_e is longer for Cu$^+$Kr than for Cu$^+$Ar. For Cu$^+$Kr, our calculated R_e (basis set C) is 0.09 Å smaller than the MCPF (self-consistent-field based modified coupled-pair functional)[17a] result, whereas D_e is about 0.18 eV larger. For Cu$^+$Ar, our CCSD(T) (basis set C) result for R_e is 0.06 Å shorter than the MCPF[17c] result, and 0.20 Å shorter than that from the CISDQ[17b] calculation. The resulting D_e value is 0.11 eV and 0.05 eV larger than from the MCPF and CISDQ theoretical methods, respectively. The resulting D_e and R_e at the HF level (basis C), however, are close to those from ref 17b, with our calculated D_e 0.03 eV larger and R_e 0.06 Å shorter than the literature values. We have larger D_e and smaller R_e in all cases, in that we have much larger basis sets.

Comparing R_e and D_e for the cationic species, Table 7, with those of the neutral species, Table 6, it is clear that the cationic species have a much smaller values of R_e and much larger dissociation energies. The difference in R_e is 1.6 Å for krypton complexes and 1.7 Å for argon complexes. D_e for Cu$^+$Kr is approximately 40 times that for CuKr, and the corresponding ratio for argon complexes is approximately 30. The differences in R_e and D_e between the cationic species and the neutral species arise from the different dominant contributions to the interaction. The binding in the neutral species is mainly from the induced dipole−induced dipole interaction, whereas the binding in the cationic species is mainly from the charge-induced dipole interaction, which is stronger.

4. Conclusions

Interatomic potential energies have been obtained for Cu^+-Ar, Cu^+Kr, CuAr, and CuKr as a function of atomic separation. The calculations were performed for a range of theoretical methods using relativistic pseudopotential basis sets with additional diffuse polarization functions and bond functions. The counterpoise correction was applied to all calculations to correct for the basis set superposition error. With the CCSD(T) result as a comparison standard, the MP2 method was shown to be in excellent agreement with a general trend.

The potential energy curves for the two neutral rare gas complexes are identical in shape, but the well-depth for the krypton complexes is greater than that for the argon molecules and the equilibrium distance for the krypton complexes occurs at smaller separations, reflecting its greater polarizability. The minima in the potential energy curves for the complexes with the copper cation occur at smaller separations, due to the fact that induction rather than dispersion forces bind the two components of the complex. In addition, the well depths are significantly greater for both cation complexes. Linear fitting of the interaction energy as a function of R^{-4} provided excellent results for the polarizabilities of the rare gas atoms. The Cu^+-Kr/Ar results are compared with the only previously reported calculations. The CuKr results deviate significantly from the one available photoionization study. This disagreement might suggest the importance of static correlation effects in calculations involving this complex.

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