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Geometries and Bond Energies of the He−MX, Ne−MX, and Ar−MX (M = Cu, Ag, Au; X = F, Cl) Complexes

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Calculations on the He···MX, Ne···MX, and Ar···MX (M = Cu, Ag, Au; X = F, Cl) complexes at the CCSD and CCSD(T) levels of theory have been carried out. The geometries of the Ar−MF complexes are in good agreement to those determined via microwave spectroscopy. The RG···MX (RG = He, Ne, and Ar) dissociation energies for these complexes have been evaluated by extrapolation to the complete basis set limit. The importance of the inclusion of diffuse functions to the determined dissociation energies of these complexes are discussed with comparison to recent work. For the He···CuF and He···AuF complexes, the dissociation energies have been found to be significant, at ≈26 kJ mol^{-1}, while the bonding in the chlorine analogues is only ≈15 kJ mol^{-1}. The bonding between the helium and the metal atoms in the He···CuF and He···AuF complexes has been investigated by using an atoms-in-molecules (AIM) analysis together with an evaluation of the dipole/induced-dipole and ion/induced-dipole interactions. This analysis has shown that the bonding in these complexes is slightly covalent in nature. For the He···AgF and Ne···MF (M = Cu, Ag, Au) complexes the dissociation energy is much smaller and the AIM analysis shows the bonding is more electrostatic in nature. Calculations have also been carried out on He···AgCl and Ne···MCl (M = Cu, Ag, Au) complexes for the first time in addition to the Ar···MX (M = Cu, Ag, Au; X = F, Cl) complexes. The RG···MCl complexes are found to be more weakly bound than the corresponding RG···MF complexes as a result of the difference in electronegativity of the halogen. For each complex, bond lengths, rotational constants, and harmonic vibrational frequencies have also been evaluated.

Introduction

It is well-known that both xenon and krypton can form stable compounds with either covalent or ionic bonds.[1] In 2000, two research groups reported finding compounds containing chemically bonded argon. The first of these, a group working in Finland, detected the insertion compound HArF in an argon matrix using infrared spectroscopy.[2] In this study they showed that the H−Ar bond is strongly covalent in nature, while the Ar−F bond is more ionic in nature. In the same year a group from Canada produced the Ar···AgX (X = F, Cl, Br) complexes and quickly followed this with studies on the Ar···CuX and Ar···AuX complexes using Fourier transform microwave spectroscopy.[3–6] For each complex they were able to determine the argon−metal bond length, which ranged from 260 pm for Ar···AgF to only 225 pm for Ar···CuF. Computational studies on these complexes showed that the argon−metal dissociation energy ranges between 19 kJ mol^{-1} for Ar···AgF to 47 kJ mol^{-1} for Ar···AuF.[4] Although the argon−metal bonding in these complexes is not as strong as those for the insertion compound HArF, which has an HArF → HF + Ar energy barrier[7] of 117 kJ mol^{-1}, the bonding is still thought to have a small covalent contribution. Analogous complexes containing Kr and Xe have also been found and the bonding between these rare gases and the coinage metal atoms is significantly stronger.[5,8–11]

So what about helium and neon? Since the discovery of HArF and Ar···AgF in 2000, there has been renewed interest in finding similar systems for helium and neon.[7,12–20] If the strength of the RG−X interaction were controlled only by the polarizability of the rare gas atoms, then the chances of having stable compounds with helium ($\alpha = 2.05 \times 10^{-25}$ cm^3) and neon ($\alpha = 3.96 \times 10^{-25}$ cm^3) is relatively improbable, given the much larger polarizability of Ar ($\alpha = 1.64 \times 10^{-24}$ cm^3). In the case of helium, however, an alternative bonding mechanism has been proposed. In the 1980s Frenking et al. proposed a donor−acceptor model to show that helium could in fact form stable chemical compounds.[21–25] In this work they proposed a set of criteria that, if met, would allow the formation of a chemical bond between helium and another species (X). The basic criterion for the formation of a covalent He···X bond is the availability of an s- or σ-hole in tandem with a sufficiently large positive charge on X. Since the helium donor−acceptor model was first published, a number of strong candidates have been put forward as stable helium-containing compounds. However, observation of these species would be somewhat difficult since the majority of the proposed species are typically exotic, highly charged ions (e.g., $HeCC^{2+}$).[25] From an experimental point of view, what is ideally wanted is a neutral species that can be generated and detected in an easy manner. A number of neutral compounds have already been put forward as good candidates. The first calculations on stable complexes containing helium were performed in 1986 by Koch et al. who investigated He···BCH and He···BeO.[26] Since 1986 there have been a number of computational studies of neutral compounds containing helium with most resulting in He···M dissociation energies ranging from 4 to 30 kJ mol^{-1}. In most cases, however, these neutral compounds have either contained a toxic metal (e.g., Be in He···BeO) or are experimentally challenging to make, such as

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TABLE 1: Bond Lengths (in pm) Calculated at the CCSD/aVQZ Level of Theory; and RG−M Dissociation Energies (kJ mol^{-1}) of the RG−MF Species (RG = He, Ne, Ar; M = Cu, Ag, Au)

			dissociation energy (D_e) RG···MX				
species	r(RG−M)	r(M−F)	aVTZ[a]	aVQZ[b]	aV5Z[c]	CBS[d]	previous work
He−CuF	167.6	173.6	25.3	26.8	27.0	27.2	
	165.9[e]	173.2[e]					25.8[f]
He−AgF	217.3	197.2	4.34	5.20	5.41	5.63	
	214.3[e]	196.7[e]					5.1[f]
He−AuF	184.0	190.5	22.6	24.6	25.1	25.6	
	184.1[e]	190.4[e]					24.9[f]
	184.0[g]	191.0[g]					24.1[g]
Ne−CuF	220.5	174.3	9.29	10.6	11.2	11.9	
	217.2[e]	173.8[e]					9.8[f]
Ne−AgF	273.0	197.9	2.87	3.34	3.67	4.02	
	270.0[e]	197.4[e]					2.7[f]
Ne−AuF	245.6	191.9	7.53	8.89	9.50	10.1	
	244.4[e]	191.7[e]					8.6[f]
	248.0[g]	192.0[g]					7.0[g]
Ar−CuF	224.6	174.3	40.7	44.4	46.1	47.8	
	221.9[h]	175.3[h]					44[i], 37[j]
Ar−AgF	258.7	197.0	19.4	22.2	23.1	24.1	14[i], 18[j]
	255.8[k]	198.6[k]					
Ar−AuF	240.8	191.5	45.5	50.4	52.3	54.3	
	239.1[l]	191.8[m]					55[i], 50[j]
CuF		174.9					
		174.5[n]					
AgF		198.2					
		198.3[n]					
AuF		192.7					
		191.8[m]					

[a] CCSD(T)/aVTZ//CCSD/aVTZ. [b] CCSD(T)/aVQZ//CCSD/aVQZ. [c] CCSD(T)/aV5Z//CCSD/aVQZ. [d] CCSD(T)-Complete Basis set limit (Halkier et al. method). [e] CCSD(T)/V5Z.[30] [f] Counterpoise corrected, CCSD(T)-complete basis set limit.[30] [g] Reference 31, bond lengths at CCSD(T)/aVTZ, D_e at CCSD(T)/aVQZ. [h] Microwave Study.[3] [i] Counterpoise corrected, MP2 with basis sets of approximately aVTZ standard.[11] [j] Counterpoise corrected, MP2 with customized basis sets of approximately aVTZ-aVQZ standard.[49] [k] Microwave Study.[4] [l] Microwave Study.[6] [m] Microwave Study.[39] [n] Microwave Study.[40]

HeO···CsF.[17,26–28] Computational studies on similar neon-containing species has shown that it is less likely than helium to form stable compounds through the donor−acceptor mechanism, since it contains occupied p-orbitals, which would result in significant repulsion effects.[24,25,29]

Since the Ar···MF (M = Cu, Ag, Au) compounds are neutral and were relatively easy to observe experimentally, it was thought that it would be of interest to extend the theoretical studies of these complexes to include the He···MF and Ne···MF complexes, with the aim of finding a suitable neutral helium-containing compound that could be easily studied experimentally. While the present paper was being written, the geometries and dissociation energies of the helium and neon complexes of the coinage metal fluorides determined at the CCSD(T) level using the correlation consistent valence basis sets of Dunning et al. were published by Zou et al.[30] Another study by Chen et al.[31] was published soon after, which considered the He−AuF and Ne−AuF complexes using similar levels of theory. We therefore compare our results with those, noting that augmentation of the basis sets with diffuse functions was not done in those studies: something that is generally found to be an important addition to basis sets when performing calculations on weakly bound complexes, and/or those involving electronegative elements, such as fluorine. We thus report the results of our study, where we have utilized the corresponding augmented valence basis sets; which allow a more complete description of the diffuse nature of the bonding within weakly bound complexes. Additionally, to provide further insight into the bonding mechanism, we have investigated both the coinage metal fluoride and chloride complexes of helium, neon, and argon.

Calculations

Calculations were carried out using the quantum chemistry software packages Gaussian03 and Molpro.[32,33] The basis sets used for He, Ne, Ar, F, and Cl were the augmented correlation consistent basis sets, aug-cc-pVXZ (X = D−5) (denoted aVDZ, aVTZ, aVQZ, aV5Z herein) of Dunning et al.[34–36] For the metals, the small-core relativistic effective core potentials, ECP10MDF, ECP28MDF, and ECP60MDF were employed for Cu, Ag, and Au, respectively, with the corresponding correlation consistent valence basis sets (aVDZ, aVTZ, aVQZ, and aV5Z).[37,38] The ground electronic states of CuX, AgX, and AuX (X = F, Cl) are closed-shell $^1\Sigma^+$ states.[39–43] The structures of each species were optimized at the CCSD level of theory using the aVDZ, aVTZ, and aVQZ basis sets described above. Single-point calculations were carried out at each geometry at the CCSD(T) level of theory, including the full counterpoise correction.[44] For each complex, a single point CCSD(T)/aV5Z energy calculation was also conducted at the CCSD/aVQZ equilibrium geometry. For each metal, all electrons not described by the effective core potential were included in the correlation treatment, whereas only the valence electrons of F, Cl and the rare gases were correlated. Extrapolation of the binding energy to the complete basis set limit using the results from the aVQZ and aV5Z basis sets was achieved using the two-point method of Halkier et al.[45] Input files for the atoms-in-molecules (AIM)[46] analysis were generated by Gaussian03 at the CCSD/aVTZ level of theory and analyzed using the XAIM package.[47] GaussView[48] was used as the visualization software throughout this study.

TABLE 2: Bond Lengths (in pm) Calculated at the CCSD/aVQZ Level of Theory; and the RG−M Dissociation Energies (kJ mol^{-1}) of the RG−MCl Species (RG = He, Ne, Ar; M = Cu, Ag, Au)

			dissociation energy (D_e)/ cm^{-1}				
species	r(RG−M)	r(M−Cl)	aVTZ[a]	aVQZ[b]	aV5Z[c]	CBS[d]	previous work
He−CuCl	175.3	205.6	15.5	17.0	17.4	17.8	
He−AgCl	226.2	228.3	3.30	4.06	4.29	4.52	
He−AuCl	197.4	220.8	11.0	12.6	13.1	13.6	
Ne−CuCl	229.5	205.9	5.94	7.12	7.77	8.46	
Ne−AgCl	274.3	228.0	2.87	3.37	3.69	4.04	
Ne−AuCl	259.3	221.4	4.97	5.93	6.47	7.04	
Ar−CuCl	229.9	206.0	32.5	36.1	37.7	39.3	33[f], 28[g]
	226[e]	207[e]					
Ar−AgCl	263.3	228.0	17.7	20.2	21.1	22.0	16[g]
	259.7[h]	228.5[h]					
Ar−AuCl	249.2	221.5	33.1	37.2	38.8	40.5	42[f], 38[g]
CuCl		206.4					
		205.1[i]					
AgCl		229.0					
		228.1[j]					
AuCl		221.9					
		219.9[k]					

[a] CCSD(T)/aVTZ//CCSD/aVTZ. [b] CCSD(T)/aVQZ//CCSD/aVQZ. [c] CCSD(T)/aV5Z//CCSD/aVQZ. [d] CCSD(T)-complete basis set limit (Halkier et al. method). [e] Microwave Study.[3] [f] Counterpoise corrected, MP2 with basis sets of approximately aVTZ standard.[11] [g] Counterpoise corrected, MP2 with customized basis sets of approximately aVTZ-aVQZ standard.[49] [h] Microwave Study.[4] [i] Microwave Study.[41] [j] Microwave Study.[42] [k] Microwave Study.[43]

TABLE 3: Ne−Ag Dissociation Energies (kJ mol^{-1}) Calculated at the CCSD(T) Level Using Different Basis Sets (see text)[a]

basis set	D_e
V5Z	2.63
wCV5Z	2.67
aV5Z	3.67
awCV5Z	3.71

[a] The full counterpoise correction has been included in each case.

TABLE 4: Rotational Constants (B_e in MHz) and Harmonic Vibrational Frequencies (in cm^{-1}) of He−MF, Ne−MF, and Ar−MF (M = Cu, Ag, Au)[a]

species	B	RG−M stretch	M−F stretch	RG−M−F bend
He−CuF	8347.3	484.8	665.1	183.2
		603[b]	673[b]	199[b]
Ne−CuF	3269.7	131.8	635.1	77.7
		74[b]	632[b]	140[b]
Ar−CuF	2168.9	200.1	644.2	112.6
	2197.0[c]	224[c]		
He−AgF	5844.5	188.3	529.2	81.2
		203[b]	531[b]	90[b]
Ne−AgF	2268.6	66.2	521.3	26.4
		68[b]	520[b]	31[b]
Ar−AgF	1604.7	125.6	531.3	64.2
	1623.1[d]	141[d]		
He−AuF	6421.6	506.1	623.3	255.9
		501[b]	620[b]	253[b]
		500[e]		
Ne−AuF	2646.4	122.2	579.5	83.6
		125[b]	577[b]	85[b]
		150[e]		
Ar−AuF	1759.2	196.5	597.6	117.8
	1775.3[f]	221[f]		

[a] Determined from CCSD/aVQZ geometry. Rotational constant and vibrational frequencies are for the average isotope. A pseudodiatomic approximation was used in the microwave studies to determine the RG−M stretching frequency. [b] CCSD(T)/V5Z.[30] [c] Microwave Study.[3] [d] Microwave Study.[4] [e] CCSD(T)/aVTZ.[31] [f] Microwave Study.[6]

Results and Discussion

Tables 1 and 2 show the results obtained for the helium and neon coinage metal fluoride and chloride complexes, respectively. For comparison, and to judge the accuracy of the calculations, predicted values of the argon coinage metal halide complexes are also shown. The values for these argon-containing complexes from the present work are similar to those from previous computational and experimental studies.[3,4,6,30,49–52]

Good agreement is observed between the geometries determined in the present study to those determined by Zou et al.,[30] which they obtained at the CCSD(T)/V5Z level (where V5Z represents the cc-pV5Z basis set, i.e., without augmentation by diffuse functions) for He, Ne, and F, and with the wCV5Z-DK, ECP28MDF_wCV5Z, and ECP60MDF_wCV5Z basis sets for Cu, Ag, and Au, respectively. We note here that the geometries determined in the present study were optimized at the CCSD level, with the agreement between those determined by Zou et al.,[30] is suggestive that the geometries are not heavily dependent on the triples contributions. However, the calculated RG···M dissociation energies are consistently higher in the present study than those determined in that work; most notably for the weakly bound Ne···AgF complex where the value determined by Zou et al. is $\approx^2/_3$ of that calculated in the present study.[30] Table 3 shows calculated counterpoise (CP)-corrected dissociation energies for the Ne···AgF complex at the CCSD/aVQZ geometry determined in the present study, using a combination of augmented and nonaugmented V5Z and wCV5Z basis sets for Ag, with the corresponding augmented and nonaugmented V5Z basis sets for He and F calculated at the CCSD(T) level. We note that the inclusion of "tight" functions (as represented by the "C" in the basis set designation) allows a more thorough treatment of the correlation of the inner valence metal electrons. Inclusion of these functions, however, appears to make an almost negligible difference in the calculated dissociation energies. It is apparent that the majority of the difference between the RG···MX dissociation energies determined in the two studies is due to the inclusion of augmented functions in the present work. These functions have the effect of better describing the long-range intermolecular forces and (more generally) regions of diffuse electron density, which are

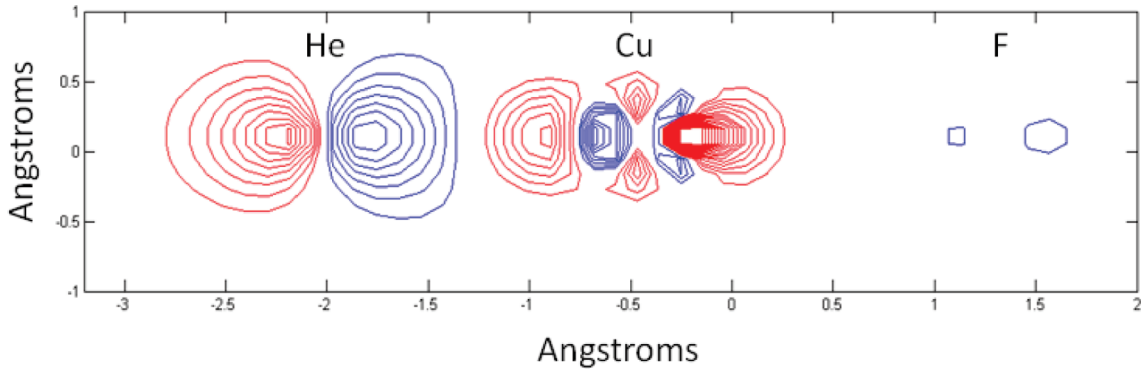

Figure 1. Contour plot of the electron difference between He−CuF and the He and CuF fragments. The blue indicates density accumulation, while the red indicates density depletion. The contours are in increments of 0.005.

TABLE 5: Rotational Constants (B_e in MHz) and Harmonic Vibrational Frequencies (in cm^{-1}) of He−MCl, Ne−MCl, and Ar−MCl (M = Cu, Ag, Au)[a]

species	B	RG−M stretch	M−Cl stretch	RG−M−Cl bend
He-CuCl	4211.7	384.8	457.2	173.0
Ne-CuCl	2016.0	94.0	415.4	31.2
Ar−CuCl	1407.5	174.9	425.2	83.3
	1441.0[b]	197[b]		
He-AgCl	2969.4	169.0	347.7	74.0
Ne-AgCl	1516.5	69.2	343.0	26.5
Ar-AgCl	1103.3	115.2	349.5	45.0
	1125.1[c]	135[c]		
He-AuCl	3018.4	336.8	401.1	160.4
Ne-AuCl	1646.9	85.7	381.2	44.04
Ar-AuCl	1202.4	161.3	388.8	75.4
	1229.9[d]	198.0[d]		

[a] Determined from CCSD/aVQZ geometry. Rotational constant and vibrational frequencies are for the average isotope. A pseudodiatomic approximation was used in the microwave studies to determine the RG−M stretching frequency. [b] Microwave Study.[3] [c] Microwave Study.[4] [d] Microwave Study.[5]

particularly important in the interactions of very weakly bound complexes involving electronegative elements. Similar comments regarding the basis set employed by Chen et al.,[31] who employed the ECP60MWB quasirelativistic pseuopotential for Au, with what appears to be the uncontracted (9s9p6d4f) ECP60MWB_MP2 basis set obtained from the Stuttgart Pseudopotential site,[53] which again does not appear to have diffuse functions; for He, Ne, and F, however, diffuse functions were employed via the standard aug-cc-pVTZ basis sets.

Basic chemical knowledge tells us that neon should form weaker bonds than argon. This is clearly confirmed for the Ne···MX dissociation energies, which are significantly smaller than those for the Ar···MX complexes. Again, as found in the Kr- and Xe-containing complexes, the RG···MX dissociation energies for Cu and Au complexes are significantly larger than those of Ag complexes owing to the more diffuse nature of the Ag atom.[8,9,11,54] The results for the He···MF (M = Cu, Ag, Au) complexes, however, indicate the possibility of chemical bonding occurring between helium and the coinage metals. The He···CuX and He···AuX dissociation energies are significantly larger than the analogous neon complexes, and only 25−50% less than the analogous argon complexes that have been observed experimentally.[3,4,6] In comparison to other neutral helium containing species studied, the dissociation energies calculated for He···CuF and He···AuF are close to that of similar systems: He···NiCO (21 kJ mol^{-1}),[20] He···BeO (22 kJ mol^{-1}),[17] and He···NiN_2 (28.6 kJ mol^{-1}).[20] Even larger systems such as $H_2C(NBeHe)_2$ and HeO-N$(CH_3)_4$F have similar He···X binding energies (∼18.5 kJ mol^{-1}).[15,27] In all these cases the He···M binding energy is significantly lower than those seen in the Ar-, Kr-, and Xe···M complexes. It should also be mentioned there are a number of helium caged systems known that show a barrier to dissociation on the order of 160 kJ mol^{-1}, but apparently the He···X interaction is not covalent in nature.[55] Of the neutral systems studied to date, the He···CuF and He···AuF complexes are probably the best candidates for detection given that similar systems, such as Ar···CuF and Ar···AuF are easily observable in the gas phase.

For He···CuF and He···AuF, the He···M bond lengths fall between the covalent and van der Waals (vdW) limits where the sum of the covalent radii, r_{cov} [r_{cov}(He) + r_{cov}(M^+)] of the He and Cu/Au atoms is 138 and 155 pm, respectively, while the sum of the vdW radii of He plus the ionic radius of the metal [(r_{vdW}(He) + r_{ion}(M^+)] gives 200 and 221 pm, respectively.[11,56–59] Listed in Tables 4 and 5 are the rotational constants and the harmonic vibrational frequencies for both sets of the RG···MF and RG···MCl (M = Cu, Ag, Au) complexes.

Charge Transfer Analysis

Figure 1 shows a contour plot from a CCSD/aug-cc-pVTZ calculation of the density accumulation (in blue) and the depletion (in red) occurring on the formation of the He···CuF complex. The plot was generated by subtracting the electron densities of the He and CuF units from the He···CuF complex. The plot shows that charge has been shifted toward the CuF unit. A comparison between ΔQ (the integrated charge transfer) for the He···MF (M = Cu, Ag, Au) complexes is given in Figure 2. This plot measures the electronic charge fluctuation with respect to the isolated fragments from left to right along

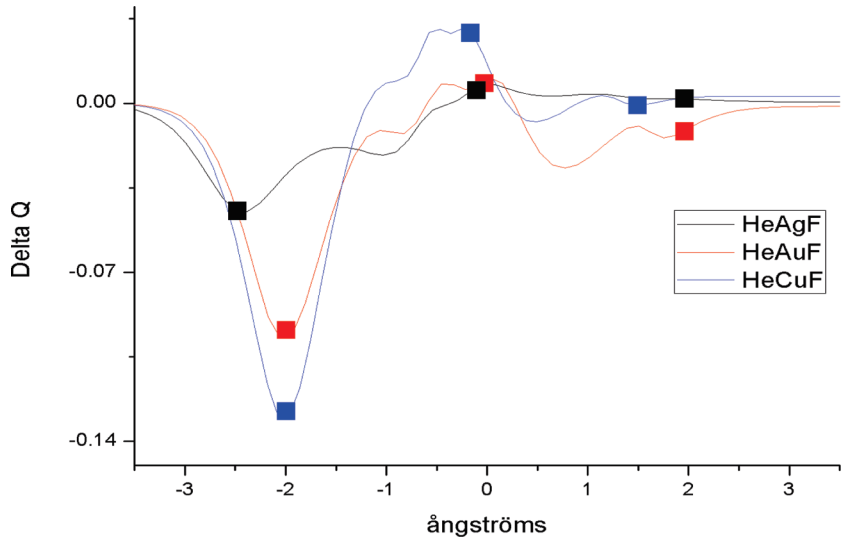

Figure 2. ΔQ plot for He−MF (M = Cu, Ag, Au). The squares indicate the location of the atoms within each complex in order of He, M, and F (from left to right).

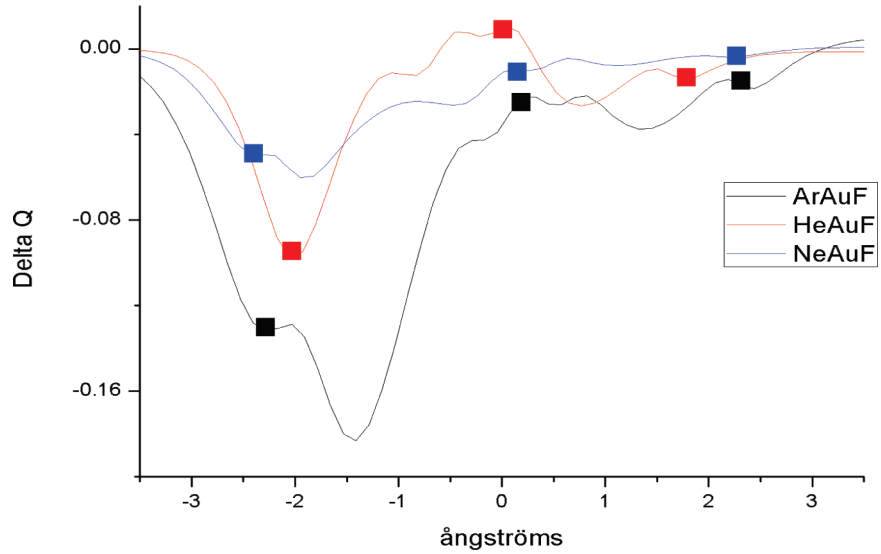

Figure 3. ΔQ plot for RG−AuF (RG = He, Ne, Ar). The squares indicate the location of the atoms within each complex in order of RG, Au, and F (left to right).

the internuclear axis.[50] The areas of the plot that show a negative slope correspond to areas of charge depletion, while those with a positive slope indicate regions of charge accumulation. Equation 1 has been used to evaluate ΔQ:

$$\Delta Q(z) = \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}y \int_{-\infty}^{z} \Delta\sigma(x, y, z')\mathrm{d}z' \qquad (1)$$

where $\Delta\sigma$ is the electron density of the RG···MF unit minus that of the RG and MF units.[50]

In Figure 2 it can be clearly seen that for the Cu and Au complexes there is significant charge transfer from the region of the helium to the metal. Figure 3 shows the same type plot as Figure 2, but for the RG···AuF (RG = He, Ne, Ar) complexes. In Figure 3 the effect from the accumulation of charge between Ar and Au in Ar···AuF can be clearly seen, which is not apparent in He···AuF. As there does not seem to be any significant charge accumulation between the helium and metal atoms, the bonding between the two might be purely electrostatic in origin, as in the case of He···BeO.[22] To test this idea, an analysis of the induction energies, similar to that carried out by Thomas et al.[11] on the Kr···AuF, Kr···AgF, and Kr···AgBr complexes, was carried out. For the ion-induced dipole interaction, eq 2 was employed:

$$E_{\mathrm{ind}} = -\left(\frac{\alpha}{4\pi\varepsilon_0}\right)\frac{q_{\mathrm{eff}}^2}{8\pi\varepsilon_0 r^4} \qquad (2)$$

where r is the RG···M internuclear distance. For the dipole−induced dipole interaction, eq 3 was used.

$$E_{\mathrm{ind}} = -2\left(\frac{\alpha}{4\pi\varepsilon_0}\right)\frac{\mu^2}{4\pi\varepsilon_0 r^6} \qquad (3)$$

where r is the distance from the RG nucleus to the center of the charge of the MX dipole ($= r_{\mathrm{RG-M}} + r_{\mathrm{MF/2}}$).

Table 6 shows the induction energies based on dipole/induced-dipole and ion/induced-dipole interactions for the RG···MF (RG = He, Ne, Ar; M = Cu, Ag, Au) complexes.

TABLE 6: Comparison of MF Dipole moments (in Debye) and Effective Atomic Charges, Induction Energies (in kJ mol^{-1}), and ab initio Dissociation Energies (in kJ mol^{-1}) of RG−MF complexes (M = Cu, Ag, Au)

complex	MX		$-E_{ind}$		
	μ^a	$q_{eff}{}^a$	μ/μ_{ind}	q_{eff}/μ_{ind}	$D_e{}^b$
He−CuF	5.77	0.69	3	9	27.2
He−AgF	6.22	0.65	1	3	5.63
He−AuF	3.4	0.37	1	2	25.6
Ne−CuF	5.77	0.69	2	6	11.9
Ne−AgF	6.22	0.65	1	2	4.02
Ne−AuF	3.4	0.37	0	1	10.1
Ar−CuF	5.77	0.69	8	22	47.8
Ar−AgF	6.22	0.65	4	11	24.1
Ar−AuF	3.4	0.37	2	5	54.3
He−Cu$^+$		1.00		10.3	10.6^d
					9.5^c
He−Ag$^+$		1.00		4.2	5.0^d
					4.7^c
He−Au$^+$		1.00		4.0	5.1^d
					4.6^c 5.0^e
He−BeO	7.1	0.84	11.9	19.2	25^d
					22^f

^{a} Taken from reference 11. ^{b} This work. Two point extrapolation using CCSD(T)/aVQZ and aV5Z results. ^{c} CCSD(T)/aV5Z.[60] ^{d} This work. Three point extrapolation using CCSD(T)/aVDZ/aVTZ and aVQZ results. ^{e} CASPT2 value.[17] ^{f} CCSD(T)/aV∞Z.[61]

There are limitations to eqs 2 and 3 and so the values in Table 6 do not take into account all the possible interactions, both attractive and repulsive, occurring in these systems; however, the numbers clearly show trends that are useful in understanding the bonding occurring in these complexes. For comparison, similar ab initio calculations to those undertaken for the RG···MX complexes have been carried out on He···M$^+$ and He···BeO [at the CCSD(T)/aVXZ X = D,T,Q level of theory and extrapolated to the CBS limit using the three-point method of Halkier et al.[45]]. The dissociation energies calculated for these species are shown in Table 6, along with the calculated inductive energies. The ab initio dissociation energies are in good agreement with those calculated in previous studies.[60,61]

As can be seen in Table 6, the induction energies do not fully explain the large RG···M dissociation energies predicted for the He···CuF and He···AuF complexes. For the copper-containing complexes the calculated induction energy is considerably higher than those containing silver and gold, which is attributable to the smaller bond length between the rare gas and copper atoms. For all but the silver-containing complexes, the difference between the calculated dissociation energy and the sum of the induction energies is positive, which implies the bonding between RG···M (RG = He, Ne, and Ar; M = Cu, Au) is slightly covalent in nature.[62] For the silver-containing complexes the RG···Ag bonding is more electrostatic in nature. For He···BeO the sum of the induction energies is greater than the predicted dissociation energy, which implies the He···Be bond is electrostatic in nature, which agrees with the conclusion reached in previous studies.[21–23,26]

Looking at the Laplacian ($\nabla^2\rho$) plots for RG···CuF in Figure 4a−c, these clearly show that for He···CuF (Figure 4a) there is hardly any distortion present (indicating the helium atom is not significantly polarized); for Ne···CuF (Figure 4b) there is no distortion present; while for Ar···CuF (figure 4c) the Ar and the Cu atoms do show some distortion which indicates incipient covalent bonding. The lack of distortion in the He···CuF Laplacian plot does seem to imply the interaction between He···Au and He···Cu is probably more electrostatic in origin than covalent, which contradicts the conclusion from the induction energy analysis. That the bonding is electrostatic in nature is further supported when comparing with He···BeO; the Laplacian plot of He···BeO given in Figure 15 of ref 22 is remarkably similar to that of He···CuF.

For He···Cu$^+$ and He···Au$^+$, the calculated induction energies explain most of the dissociation energy, which indicates

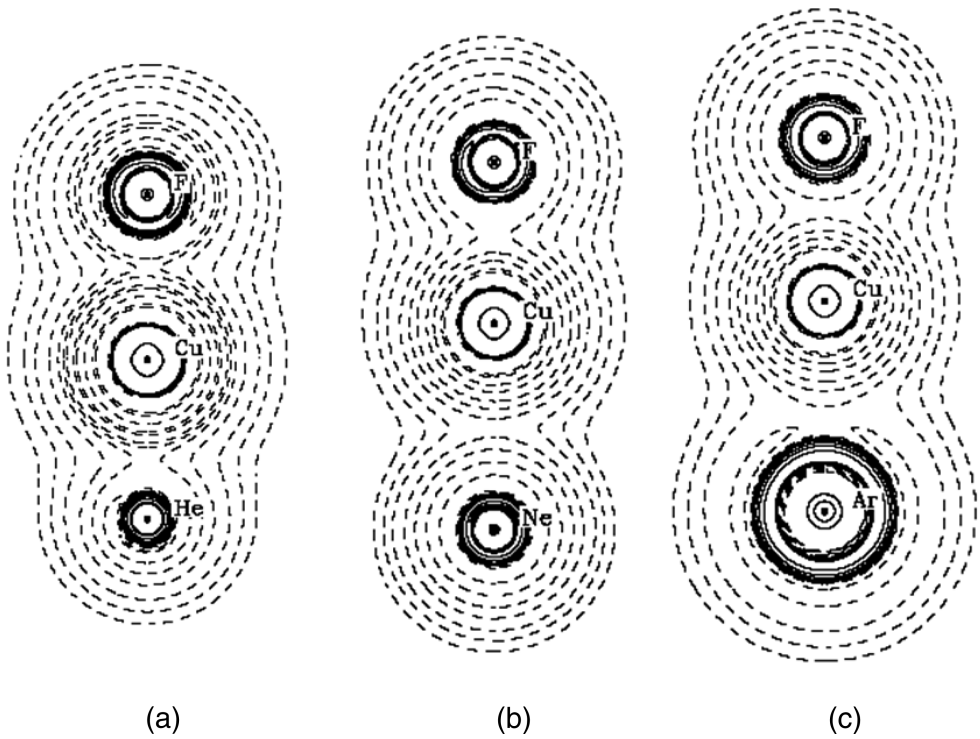

Figure 4. Laplacian ($\nabla^2\rho$) plot of (a) He−CuF, (b) Ne−CuF, and (c) Ar−CuF. The contours are ±0.02, ±0.04, ±0.08, ±0.2, ±0.4, ±0.8, ±2, ±4, ±8, ±10. The dashed lines indicate density depletion, while the solid lines indicate accumulation of density.

TABLE 7: AIM Analysis of the Rare Gas-Metal Bond Critical Point (BCP) at the CCSD/aVTZ Level of Theory: Electron Density ρ (ea_0^{-3}), Laplacian Concentration $\nabla^2\rho$ (ea_0^{-5}), and Energy Density E_d (hartree a_0^{-3})

species	ρ	$\nabla^2\rho$	E_d
He−CuF	0.069	0.537	−0.0103
Ne−CuF	0.026	0.162	0.0014
Ar−CuF	0.059	0.300	−0.0135
He−AgF	0.027	0.159	0.0001
Ne−AgF	0.010	0.049	0.0011
Ar−AgF	0.038	0.168	−0.0038
He−AuF	0.071	0.486	−0.0094
Ne−AuF	0.021	0.114	0.0011
Ar−AuF	0.062	0.272	−0.0130
He−CuCl	0.057	0.411	−0.0064
Ne−CuCl	0.023	0.158	0.0016
Ar−CuCl	0.053	0.256	−0.0107
He−AgCl	0.023	0.131	0.0009
Ne−AgCl	0.013	0.070	0.0014
Ar−AgCl	0.034	0.146	−0.0030
He−AuCl	0.049	0.314	−0.0034
Ne−AuCl	0.017	0.105	0.0018
Ar−AuCl	0.052	0.221	−0.0085

the bonding in these cations is mainly electrostatic in nature. Following Frenking's donor−acceptor model,[21–25] both species have a +1 charge and a suitable "hole" present into which the helium can donate electron density into the LUMO on M^+. The LUMO (an empty s orbital) for Cu^+ and Au^+ is very low in energy, −6.50 and −7.43 eV, respectively, while the HOMO−LUMO gap is 15.35 eV for Cu^+ and 13.33 eV for Au^+ (at the CCSD/aVTZ level of theory), which means interaction with the 1s orbital on the helium should be favorable. However, the He···M^+ bond lengths are longer than those determined for the He···MX complexes: since the d-orbitals are all filled for both Cu^+ and Au^+ there will be significant repulsion effects from the dσ orbital, which probably negates the favorable effects from the charge and the low-lying LUMO. CuF and AuF, are also closed-shell systems and the LUMO energy is −0.43 and −0.73 eV, respectively (at the CCSD/aVTZ level of theory); the HOMO−LUMO gap for CuF and AuF is smaller than Cu^+ (CuF ≈ 11.4 eV) and Au^+ (AuF ≈ 10.6 eV). In CuF and AuF, the metals also have less positive charge associated with them (see Table 8) compared to Cu^+ and Au^+. So, why do He···MF (M = Cu, Au) complexes have a higher He···M dissociation energy than He···M^+? First, the LUMO on the MF (M = Cu, Au) unit has a significant lobe pointing along the internuclear axis toward the rare gas that is not seen in Cu^+ and Au^+; the direction of the lobe would enhance the metal's interaction with the helium 1s orbital (see Figure 5). Second, the presence of fluorine in the MF unit is very important: because of its high electronegativity it pulls electron density away from the metal atom, reducing the repulsion effects resulting from the σ-MOs, which will allow the helium atom to get closer to the metal atom. Lastly, the smaller HOMO−LUMO gap found for CuF and AuF may also enhance the He···Cu and He···Au interactions.

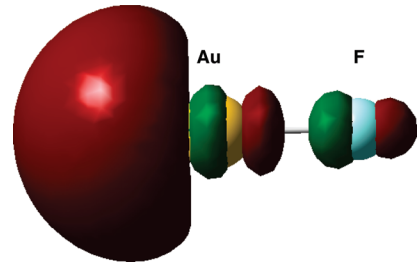

Figure 5. The LUMO of AuF with an isovalue of 0.04e.

For the chlorine analogues the lower electronegativity of Cl results in less electron density being kept away from the metal; therefore the repulsive effects owing to the σ-MOs of MCl will be higher than those in MF, resulting in the observed longer He···M bond lengths in the He···MCl complexes. The effect of electronegativity of the X atom in MX can also be seen in the Ar···CuX complexes (X = F, Cl, Br) where the Ar···Cu binding energy decreases with the decrease in the electronegativity of the halide.[3]

Neon has occupied p-orbitals and therefore the repulsion effects from π-MOs on the MX (X = F, Cl) unit will be significant. As a result of these repulsion effects, the neon atom cannot get close to the metal atom and so the dissociation energy between the neon and the coinage metal halide is significantly less than that found for He···MF complexes. Argon also has occupied p-orbitals like neon, but it has a larger polarizability that ameliorates the repulsion effects from π-MOs on the MX unit (X = F, Cl) and results in a higher Ar···M binding energy.

AIM and Population Analysis

To look in more detail at the nature of the bonding in He···MX and Ne···MX (M = Cu, Ag, Au; X = F, Cl), an atoms-in-molecules (AIM)[46] analysis was carried out on each

TABLE 8: Natural Bond Orbital Analysis and Charges for, He, MF, and He−MF (M = Cu, Ag, Au)[a]

	He + CuF	HeCuF	He + AgF	HeAgF	He + AuF	HeAuF
He						
q^b	0.00	0.06	0.00	0.02	0.00	0.07
n_s	2.00	1.93	2.00	1.97	2.00	1.92
M						
q	0.83	0.74	0.85	0.81	0.68	0.60
n_s	0.26	0.36	0.18	0.22	0.53	0.68
$n_{p(\sigma)}$	0.03	0.05	0.03	0.03	0.06	0.04
$n_{p(\pi)}$	0.06	0.08	0.04	0.05	0.02	0.07
$(n-1)_{d(\sigma)}$	1.86	1.81	1.92	1.90	1.73	1.64
$(n-1)_{d(\pi)}$	3.97	3.96	3.95	3.95	3.94	3.93
$(n-1)_{d(\delta)}$	3.98	3.98	3.96	3.96	3.95	3.95
F						
q	−0.83	−0.80	−0.85	−0.83	−0.68	−0.67
n_s	1.97	1.96	1.98	1.98	1.97	1.95
$n_{p(\sigma)}$	1.87	1.86	1.87	1.87	1.72	1.73
$n_{p(\pi)}$	3.95	3.94	3.96	3.96	3.96	3.95

[a] The CCSD/aVTZ level of theory was used. [b] The units of q are fractions of the elementary negative charge e.

TABLE 9: Natural Bond Orbital Analysis and Charges for He, MCl, and He−MCl (M = Cu, Ag, Au)[a]

	He + CuCl	HeCuCl	He + AgCl	HeAgCl	He + AuCl	HeAuCl
He						
q^b	0.00	0.04	0.00	0.01	0.00	0.04
n_s	2.00	1.94	2.00	1.97	2.00	1.94
M						
q	0.76	0.71	0.77	0.74	0.53	0.49
n_s	0.28	0.37	0.25	0.28	0.61	0.69
$n_{p(\sigma)}$	0.02	0.02	0.02	0.02	0.02	0.02
$n_{p(\pi)}$	0.04	0.04	0.03	0.03	0.05	0.05
$(n-1)_{d(\sigma)}$	1.90	1.86	1.93	1.92	1.80	1.75
$(n-1)_{d(\pi)}$	3.94	3.94	3.93	3.93	3.92	3.92
$(n-1)_{d(\delta)}$	3.95	3.95	3.94	3.94	3.93	3.93
Cl						
q	−0.76	−0.74	−0.77	−0.76	−0.53	−0.53
n_s	1.95	1.94	1.96	1.95	1.94	1.93
$n_{p(\sigma)}$	1.75	1.75	1.75	1.75	1.53	1.55
$n_{p(\pi)}$	3.87	3.88	3.88	3.88	3.88	3.88

[a] The CCSD/aVTZ level of theory was used. [b] The units of q are fractions of the elementary negative charge e.

species using the aVTZ basis set and the CCSD densities. Table 7 shows the AIM analysis at the rare gas-metal bond critical point (BCP) for each species including the Ar···MX (M = Cu, Ag, Au; X = F, Cl) complexes. The ρ(the charge density), $\nabla^2\rho$ (the Laplacian), and E_d (the electronic energy density) values are listed in Table 7 and give an indication of the nature of the bonding occurring in these complexes. For the He···CuF and He···AuF complexes ρ is positive and E_d is slightly negative, which implies that the He···M bond is more covalent in nature, which is the same as the Ar···MF (M = Cu, Au) complexes. For the Ne···MF complexes, ρ is positive, but E_d is also slightly positive, indicating that the Ne···M bond is more electrostatic in nature. The values of E_d for these complexes are close to zero, which suggests that the bonding occurring between the rare gases and the coinage metals is on the borderline between an electrostatic and covalent bond. A similar trend is seen for chlorine analogues, but the values of ρ, $\nabla^2\rho$, and E_d are smaller in magnitude, further confirming the weaker RG···M bonding in these complexes.

Natural bond orbital (NBO) analyses have also been carried out on He···MX species to investigate the amount of charge that has been transferred from the rare gas to the metal. The results of these analyses can be seen in Tables 8 and 9 for the He···MF and He···MCl complexes, respectively, along with the charges on each atom. For He···AuF and He···CuF there is a donation of charge from helium to the metal of, ∼0.07e and ∼0.06e, respectively. Smaller amounts of charge transfer are observed for the He···AuCl and He···CuCl complexes, where a donation of ∼0.04e from the helium to the meal is observed in both complexes, in line with expectations from the longer He···M bond lengths and lower dissociation energies of the He···MCl complexes. As with all the silver complexes of this type, the donation of charge from the rare gas to the silver atom is very small; in the case of He···AgF there is only a donation of 0.02e. In the Ne···MX species, the charge transfer from the neon to the metal was found to be negligible.

Conclusion

High-level ab initio calculations have been carried out on the RG···MX (RG = He, Ne, Ar; M = Cu, Ag, Au; X = F, Cl) complexes. The present calculations are at the highest level to date and have shown that the RG···M dissociation energies are very sensitive to the basis set employed, and in particular diffuse functions need to be included. In line with experimental observations of the Ar···CuX (X = F, Cl, Br) complexes,[3] the He···MCl and Ne···MCl complexes are more weakly bound than the corresponding fluoride complexes. This study has also shown that the bonding between helium and the MF unit in He···CuF and He···AuF is probably slightly covalent in nature. The bonding mechanism is consistent with the donor−acceptor model proposed by Frenking et al.,[21–25] where, with both a suitable LUMO and a significant partial charge on the acceptor group, a partial covalent bond can be formed with helium. The bonding between neon and the MF unit for the Ne···MX complexes has been found to more electrostatic in nature, owing to stronger repulsion between the Ne 2p orbitals and the π-MOs on the MX unit. The bonding in complexes such as Ar···CuF and He···CuF is difficult to rationalize fully, and as Koch et al. indicated in their work[26] on the He···BeO complex, formation of a He···X "bond" is a delicate balance between orbital energy spacings, electron density, the nature of the acceptor group, and the dipole moment leading to the dipole/induced-dipole interaction. As a result, different types of analyses suggest different conclusions regarding whether chemical bonding is occurring or not with these complexes. For the He···CuF and He···AuF complexes, there is no overall proof that a covalent bond is being formed, although some of the evidence indicates that there is; consequently, more studies, both theoretical and experimental, need to be carried out on these complexes. As the nature of the bonding occurring in these systems is still inconclusive the use of the term "bonding" might need to be reconsidered in these cases.

Although the interactions in the He···CuF and He···AuF complexes are weaker than that seen in the Ar···MF(M = Cu, Au) complexes, it is stronger than that seen in the Ar···AgF, which has been easily detected experimentally using Fourier transform microwave spectroscopy.[4] For the chlorine-containing species, the bonding in He···CuCl and He···AuCl is much smaller than that calculated for the argon analogues, which is a result of the difference in the electronegativity of the fluorine compare to the chlorine. Based on this, the He···CuF and He···AuF complexes should be readily observable using spectroscopic methods, while the chlorine analogues should also be observable but may be harder to generate. It is hoped that the present study will generate interest in these complexes and hopefully aid in their spectroscopic detection.

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