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Evidence for Emergent Chemical Bonding in Au^+−Rg Complexes (Rg = Ne, Ar, Kr, and Xe)

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Evidence is presented that there is a clear covalent component in the bonding of Au^+ to Kr and Au^+ to Xe, with some evidence that there may be such bonding between Au^+ and Ar; for Au^+ and Ne, there is no such evidence, and the bonding seems to be entirely physical. A model potential analysis shows that when all attractive inductive and dispersive terms out to R^{-8} are properly included in the Au^+−Ne case, with an Ae^{-bR} Born−Mayer repulsive term, essentially all the bonding in Au^+−Ne can be rationalized by physical attraction alone. This is consistent with a natural bond order (NBO) analysis of the Au^+−Ne *ab initio* wavefunctions, which shows the charge on Au^+ to be very close to 1.0. In contrast, similar model potential and NBO analyses show quite clearly that physical interactions alone cannot account for the large bond energy values for the Au^+−Kr and Au^+−Xe complexes and are consistent with covalent contributions to the Au^+−Kr and Au^+−Xe interactions. Au^+−Ar is seen to lie on the borderline between these two limits. In performing the model potential analyses, high-level *ab initio* calculations are employed [CCSD(T) energies, extrapolated to the complete basis set limit], to obtain reliable values of R_e, D_e and ω_e as input. A comparison of the gold−Xe bond distances in several solid-state Au(I, II and III) oxidation-state complex ions, containing "ligand" Xe atoms, prepared by Seppelt and co-workers, with that of the "free" Au^+−Xe gas-phase ion is made, and a discussion of the trends is presented.

I. Introduction

Recent experimental evidence has shown that the Xe atom can bind chemically as a ligand in transition metal coordination complexes.[1−5] The characterization,[2] reported in 2000 of a stable square planar coordination complex, $Au^{2+}(Xe)_4$ (with two $Sb_2F_{11}^-$ counterions), showed definitively that Xe can indeed function as a classical ligand. Subsequent work has led to the characterization[3,4] of the similar complexes $(F_3As)Au^+(Xe)$, *cis*-$Au^{2+}(Xe)_2$, *trans*-$(F^-)Au^{3+}(Xe)_2(SbF_6^-)$ and $(Xe)Hg^{2+}(SbF_6^-)$, again with $Sb_2F_{11}^-$ counterions. The *trans*-$Au^{2+}(Xe)_2$ complex was also prepared, with SbF_6^- as the counterion.[4] Other examples of Xe binding weakly as a ligand are for the complexes $M(CO)_5Xe$ (M = Cr, Mo, W), $Re(Cp)CO(PF_3)Xe$, $Re(Cp)(CO)_2Xe$, $Rh(Cp)(CO)_2Xe$, and $Mn(Cp)(CO)_2Xe$ which have been prepared in solid rare-gas matrices, in liquid rare gases, and in the gas phase.[1] Rare gas complexes of Au^{2+} have also been prepared in the gas phase.[6]

Of course, the simplest possible interaction of Xe as a ligand is with a metal ion in the gas phase, in singly charged M^+−Rg diatomic species. There is now an extensive set of reliable *ab initio* and experimental data for the potential curves of M^+/Rg diatomic complexes, where M = metal atom, and Rg = rare-gas atom.[7−20] One of the interesting original questions about the bonding in such M^+/Rg complexes[7,21−23] was whether it is entirely physical, that is the attractive forces are due only to the leading, strong, $1/R^4$-dependent ion-induced dipole term (plus other induction and dispersion attractive terms dependent on $1/R^6$, $1/R^7$, $1/R^8$, etc.).[7] An alternative is that some covalent contribution occurs at shorter distances, as the Rg atom begins to function as a ligand and thus binds in a classical coordinate-covalent manner with the M^+ ions. Of course, such a sharp demarcation does not exist in reality, but it is useful when considering such interactions, to have such limiting definitions in mind.

Breckenridge and co-workers have shown previously[7−9] that when all physical terms out to $1/R^8$ are properly included, almost all available data thought reliable up to 2001 for M^+−Rg potential curves could be explained adequately without having to invoke extra covalent forces. However, there were a few known exceptions,[7] the major one being the strongly bound Au^+−Xe complex,[7] for which a quite high-level *ab initio* relativistic potential curve had been calculated by Pyykkö and co-workers.[23] It was tentatively concluded[7] that the Xe atom may have substantial extra covalent attraction for the Au^+ ion; i.e., the interaction cannot be accounted for simply by physical terms alone, as Pyykkö and co-workers had originally suggested in their papers.[21,23]

Recently, we have calculated,[20] at comparably high levels, the *ab initio* curves for all of the Rg complexes of the Au^+ ion. To obviate errors in the *ab initio* treatment, we extend these calculations to the basis set limit in the present work and use these data to examine if covalent interaction is required to explain the strong bonding observed for some of these complexes.[20] In this paper, we apply the Breckenridge model potential analysis[7] to the Ne, Ar, Kr, and Xe interactions with

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Au^+. In addition, we examine carefully the *ab initio* electron density near the R_e values of these complexes,[20] to see if there is mixing of atomic orbitals that would indicate the beginnings of covalent bond formation, and how the extent of that mixing depends on the Rg atom. It is of course an intriguing general question as to when physical attraction merges into covalent attraction in weakly bound molecules, and these $Au^+{-}Rg$ ionic complexes present a unique opportunity to examine this question.

A complete set of CCSD(T)/aug-cc-pV5Z potential curves (employing small-core effective core potentials, ECPs, for the heavier atoms) for the $Au^+{-}Rg$ complexes (Rg = He−Rn) calculated by us have been published earlier.[20] A careful comparison of the whole set of coinage-metal-cation/Rg curves to available experimental and previous *ab initio* calculations led us to conclude that these curves were probably the best set of potential curves available, and by extension, also for the $Au^+{-}Rg$ complexes. The potentials were somewhat deeper than the ones reported originally by Pyykkö,[21] but the subsequent one reported by him and Schröder et al.,[23] for $Au^+{-}Xe$ was in very good agreement with that of ref 20. (Although there is a more-recent density functional theory study by Pyykkö and Runeberg,[24] the CCSD(T) calculations of ref 23 are the more reliable.) Since the completion of the work in ref 20, we learned[25] of different valence basis sets to be used with small-core ECPs.[26] In the present work, therefore, we have employed small-core ECPs for Kr, Xe and Au together with the appropriate aug-cc-pV*X*Z valence basis sets, with the standard all-electron aug-cc-pV*X*Z basis sets for Ne and Ar (X = Q, 5). We then used the two-point extrapolation procedure of Helgaker and co-workers,[27,28] to obtain results at the basis set limit. For each species, we performed a scan of the curve covering the repulsive wall, the minimum, and up to 6 Å, with the two basis sets, correcting for basis set superposition error pointwise, employing the full counterpoise correction. We then extrapolated the pair of interaction energies at each R to obtain a "complete basis set", CBS, curve. This curve was then input into LEVEL[29] to obtain spectroscopic parameters: R_e, D_e were read from the output; ω_e and $\omega_e x_e$ were obtained from least-squares fitting the energies of the lowest three vibrational levels to the standard Morse potential energy expression. These CBS values (except for $\omega_e x_e$) were then used in the model potential analysis. MOLPRO[30] was employed for all of the above calculations. In the CCSD(T) calculations, care had to be taken regarding which electrons should be included in the core, and which were correlated, owing to the overlap of the Au^+ and Rg orbitals for the lighter species—a full description of this is given in ref 20, and the same methodology was used herein.

Finally, a natural bond order (NBO) analysis[31] was performed, as described below, using Gaussian 03.[32]

(Note that we do not consider $Au^+{-}Rn$ in the present work, because reliable higher-order electrostatic terms are not available; in addition, we omit $Au^+{-}He$, because it will be included in a future paper, where the "helium anomaly" will be discussed.)

II. Results

A. Potential Curves of $Au^+{-}Rg$ Complexes (Rg = Ne−Xe). Shown in Table 1 are the R_e, ω_e, $\omega_e x_e$, k and D_e values obtained from these potential curves (where these terms are defined in the Table). Note that for $Au^+{-}Xe$, the values are in extremely good agreement with those obtained from the highest-level *ab initio* calculation of Pyykkö and co-workers.[23] In addition, the potentials are all slightly deeper than those reported in ref 20, with slightly shorter R_e values, and slightly higher ω_e values, but otherwise are in good agreement with those values.

TABLE 1: *Ab Initio* D_e, R_e, ω_e and k Values for $Au^+{-}Rg$[a]

Rg	R_e/Å	D_e/cm^{-1}	ω_e/cm^{-1} [b]	$\omega_e x_e$/cm^{-1}	k/N m^{-1}	ref
Ne	2.73	565	83.4			20
	2.692	619	90.7	3.74	8.88	this work
Ar	2.53	3745	160			20
	2.500	4016	166.5	1.80	54.2	this work
Kr	2.55	6155	148.3			20
	2.531	6489	153.1	0.91	81.2	this work
Xe	2.57	10600	149			23
	2.61	10063	151.1			20
	2.598	10529	154.7	0.57	111.0	this work

[a] R_e is the equilibrium internuclear separation, D_e is the well depth, ω_e is the harmonic vibrational frequency, and k is the harmonic force constant. [b] The isotopes used to calculate ω_e values were ^{197}Au, ^{20}Ne, ^{40}Ar, ^{84}Kr, ^{132}Xe.

B. Model Potential Analysis Employing the Values in Table 1. We now analyze the data in Table 1 using the long-range-forces model potential for $M^+{-}Rg$ species, proposed by Bellert and Breckenridge.[7] All the attractive terms out to R^{-8} are included in the potential, and the Born-Mayer repulsive term of the form Ae^{-bR} is used. This yields a model potential energy, $V(R)$, of the form[7]

$$V(R) = -\frac{\alpha_{RgD}Z^2}{2R^4} - \frac{C_6}{R^6} - \frac{\alpha_{RgQ}Z^2}{2R^6} + \frac{B_{Rg}Z^3}{R^7} - \frac{C_8}{R^8} - \frac{\alpha_{RgO}Z^2}{2R^8} - \frac{\gamma Z^4}{24R^8} + Ae^{-bR} \quad (1)$$

where Z is a fitted parameter, representing the charge on the Au^+ ion; α_{RgD}, α_{RgQ}, and α_{RgO} are the dipole, quadrupole, and octopole polarizabilities of the Rg atom; B_{Rg} (which has a *negative* value) is the dipole−dipole−quadrupole hyperpolarizability of the Rg atom; γ is the higher-order second dipole hyperpolarizability of the Rg atom; and C_6 and C_8 are Z-independent coefficients representing the first (random-dipole/induced-dipole) and second (random-dipole/induced-quadrupole, random-quadrupole/induced-dipole) terms in the dispersion interaction. The higher-order B_{Rg} term is due to the dipole moment component induced on the Rg atom by the product of the electric field strength gradient and the electric field strength. The higher-order γ term is due to the dipole moment component on the Rg atom induced by the electric field strength cubed. The dispersion coefficients are calculated by (i) the Slater−Kirkwood approximation[33,34] for the C_6 coefficients and (ii) a similar approximation derived by Koutselos and Mason[35] for the C_8 coefficients. Note that the value of Z will artificially increase if the physical model fails, to compensate for the increased attraction.

By differentiating this model equation twice, one can generate two more equations.[7] The resulting first-derivative equation (set to zero) locates the potential energy minimum, $-D_e$ (at R_e), and the resulting second-derivative equation describes the curvature of the potential (related to ω_e and the vibrational force constant, k) at R_e. If the R_e, D_e, and ω_e values of the particular state of the diatomic ion are known, or can be reliably estimated, then the three equations can be solved simultaneously[7] to yield a value for Z (which is the effective charge required to impose purely physical interactions), and the two constants, A and b, which represent the repulsive term, Ae^{-bR}. (The three parameters R_e, D_e, ω_e were chosen[7] because they accurately describe the "depth" and "shape" of the potential curve near its minimum. They are also the most generally available spectroscopic parameters.)

TABLE 2: Values of *Z*, *b*, and *A* Calculated by Applying the Undamped Model Potential Analysis to the Data in Table 1 (Damped Values in Parentheses; See Text)

	Z	A (cm^{-1})	b ($Å^{-1}$)
Au^+-Ne	1.08 (1.08)	9.39×10^7 (7.17×10^7)	4.49 (4.44)
Au^+-Ar	1.23 (1.24)	1.90×10^8 (9.93×10^7)	4.24 (4.08)
Au^+-Kr	1.32 (1.33)	2.52×10^8 (1.13×10^8)	4.08 (3.88)
Au^+-Xe	1.42 (1.45)	2.72×10^8 (9.16×10^7)	3.76 (3.49)

The values of α_{RgD}, α_{RgQ}, α_{RgO}, B_{Rg}, and γ_{Rg} are all reasonably well-known[7] from experiment or *ab initio* calculations. Values of α_{Au^+D} (the dipole polarizability of Au^+), α_{Au^+Q} (the quadrupole polarizability of Au^+) and N (the effective number of outer-shell electrons) are also required, however, to calculate the C_6 and C_8 coefficients;[7,33,34] N was taken[7] to be 10, α_{Au^+D} was taken to be[7] 1.74 ± 0.10 Å^3, and α_{Au^+Q} was estimated[36,37] to be 2.8 ± 0.5 Å^5. Tests by us have shown that only very small changes in Z occur, even if the errors in these values were twice as large.

The main idea[7] of the Breckenridge model potential analysis is that if the model potential correctly describes the bonding, Z should be close to 1.00, and covalent effects are thus quite minor, if present at all. For almost all cases studied in ref 7, $Z = 1.00 \pm 0.10$ and this was taken to be evidence that the bonding in most well-characterized M^+-Rg complexes (in 2001) was essentially physical in nature.[7] On the other hand, if Z turns out to be substantially greater than 1.0, it is taken as evidence that the purely physical terms in the model potential are insufficient to explain the strength of the bonding and thus the "fit" parameter Z necessarily rises unphysically to account for the extra covalent attraction. For only a few cases, notably Au^+-Xe, was that true when ref 7 was published.

The results of applying this model potential analysis to the data in Table 1 are shown in Table 2. The values shown were calculated by solving the three equations, noted above, for Z, A, and b employing the MAPLE program.[19]

The original version of the Breckenridge model potential[7] did not contain so-called damping functions,[19] which allow for damping of the purely long-range attractive forces at shorter ranges, where the electron clouds of the M^+ ion and the Rg atom interpenetrate. Bellert and Breckenridge[7] intentionally made no attempt to include such damping functions, both because of simplicity in comparing many M^+/Rg diatomic complexes and because there has in the past been some discussion regarding the correct mathematical form of such functions.[7]

Because the Tang-Toennies damping factors have been employed by many workers,[19] we also examined the effect of including such damping functions, $f_n(R)$, in this work. These have the form

$$f_n(R) = 1 - \exp(-bR)\sum_{k=0}^{n}\frac{[bR]^k}{k!} \qquad (2)$$

where n is the modulus of the exponent of R in the long-range term that is to be damped and b is taken to be the same value as that in the Born−Mayer potential. The equations with damping terms were set up in exactly the same manner as noted above, and solved for A, b and Z, again employing MAPLE.[19] Shown in Table 2, in parentheses, are the values of A, b, and Z obtained when damping functions are included. It is obvious that the effects on Z of "damping" are quite minor for these complexes (<4% change).

We have previously published[19] a similar model-potential analysis of very accurate *ab initio* potential curves of Alk^+-Rg complexes, where Alk^+ = alkali-metal ion. The derived model potentials quite adequately reproduced the *ab initio* potential curves over large ranges of the internuclear distances,[19] from fairly large R all the way to R values on the inner walls of the potential curves substantially above the dissociation energy. This was, of course, expected for these "baseline" cases, where chemical ligand-type attractive forces are expected to be quite small.[7,19] However, it was found[19] that the calculated Z values for Alk^+-Rg complexes were consistently just slightly greater than 1.00 (usually less than 1.05, with the highest value being 1.09 for Li^+-Xe). Although a combination of small effects could not be ruled out, a careful analysis of these results[19] led to a tentative conclusion that $Z > 1.0$ was probably not attributable to extra covalency, but a result of the simple model potential treating the induced dipoles on the Rg atoms as being infinitely small points centered exactly at the Rg nuclei (which is only valid at very large R), instead of (more accurately) representing the finite shift of Rg electronic density toward the Alk^+ ions near D_e.[19] In any case, it appears that one should not conclude from such model potential analyses that if the calculated Z value is between 1.0 and roughly 1.1 that any covalent forces are needed to explain the bonding in M^+-Rg complexes.

On the basis of the results for the Alk^+-Rg complexes, we thus propose that only if the derived model potential Z value is above 1.1 should one suspect the involvement of covalent contributions to M^+-Rg bonding. (See below for *ab initio* evidence consistent with this postulate.)

As can be seen from Table 2, the derived Z value for Au^+-Ne is below 1.1, consistent with only physical interactions, as one might expect for such an unlikely ligand as Ne, which has a very high ionization potential of 21.6 eV (compared to 15.8, 14.0, and 12.1 eV for Ar, Kr, Xe), and is apparently a "true" inert gas which does not like to "donate" its electron density to M^+ ion orbitals, even with the Au^+ ion. For the other three rare gases, however, Z is well above 1.1, rising in the sequence Ar < Kr < Xe, and is especially high for Au^+-Kr and Au^+-Xe. (Note that for $Z > 1.3$, the induction terms in eq 1 must rise to quite high values to reproduce the large D_e values artificially, because they depend on Z^2, Z^3 and Z^4.) One possible physical reason for Z being so high for the Au^+-Ar, Au^+-Kr and Au^+-Xe cases is that higher-order attractive R^{-n} terms with $n > 8$ are still important. Shown in Table 3 are the effects on Z (while reoptimizing A and b) of successively deleting terms in eq 1. As can be seen from the trends, there is a large effect from the addition of the R^{-6} terms to the ion/induced-dipole term, but the effect of addition of the R^{-7} and R^{-8} terms is smaller. Thus, the addition of higher-order terms beyond R^{-8} to eq 1 will probably decrease Z slightly, but certainly not to values below 1.1. Also, damping, which increases Z by decreasing the magnitude of the attractive terms, will be more and more important as n increases beyond $n = 8$.

An earlier claim by Read and Buckingham,[22] that the bonding in Au^+-Xe was probably entirely physical in nature has been shown to be invalid.[7] Using an equation similar to eq 1 with $Z = 1$ and with a repulsion terms of the form A/R^n, they claimed they could rationalize an earlier lower-level *ab initio* calculation of $D_e(Au^+-Xe)$ by Pyykkö[21] of 7340 cm^{-1}. However, to do so required a completely unphysically steep repulsive term of approximately A/R^{19}. An overlay[22] of their model potential curve to the *ab initio* one shows clearly that at large R, the model curve is very much less attractive, and at small R, very much more repulsive than the *ab initio* curve. This indicates that their model potential was actually unsuccessful in representing even

TABLE 3: Effects on Z of Successively Deleting Various Terms in Eq 1 (Damped Values in Parentheses)

	Au^+-Ne	Au^+-Ar	Au^+-Kr	Au^+-Xe
all terms	1.08 (1.08)	1.23 (1.24)	1.32 (1.33)	1.42 (1.45)
delete all R^{-8} terms	1.16 (1.16)	1.32 (1.32)	1.41 (1.42)	1.52 (1.53)
delete all R^{-8}, R^{-7} terms	1.17 (1.18)	1.36 (1.36)	1.47 (1.47)	1.60 (1.60)
delete all R^{-8}, R^{-7}, R^{-6} terms	1.40 (1.40)	1.57(1.57)	1.68 (1.68)	1.81 (1.81)

that Au^+-Xe potential curve. Application of their model potential to the current, highest-level potential curve for Au^+-Xe would be completely unsuccessful, and would not be able to reproduce the D_e value of 10,529 cm^{-1}. The failure of the Read–Buckingham model for Au^+-Xe, and the high values of Z obtained from the model potential analysis with our eq 1, suggests to us the possibility that increasing covalent ligand effects are present for all the Ar, Kr, Xe complexes of Au^+. This will be discussed further in the below.

C. Natural Bond Order (NBO) Analysis. We performed NBO analyses for the four Au^+-Rg diatomics under consideration, where we (owing to technical difficulties with the larger basis sets) employed the LANL2DZ basis set within Gaussian 03, which corresponds to a D95V[38] basis set for Ne, but the Los Alamos ECP on the other atoms, with a double-ζ basis set.[39-41] These basis sets are clearly smaller than those employed to obtain the CBS results herein; however, if anything, we would expect the NBO results with these smaller basis sets to *underestimate* the interaction, as deduced from the increased of the dissociation energy as the basis set is enlarged. The analyses were performed on the coupled-cluster density, and yielded the NBO partial charges as follows: $Au^{+0.96}-Ne^{+0.04}$, $Au^{+0.94}-Ar^{+0.06}$, $Au^{+0.88}-Kr^{+0.12}$, and $Au^{+0.79}-Xe^{+0.21}$. Mulliken population analyses indicated much higher proportions of charge transfer (consistent with observations by Pyykkö)[21] but are likely to be unreliable for such systems. A more-detailed analysis of the electron density may be summarized in the following series of "natural electron configurations":

Au^+-Ne: Au: $[\text{core}]6s^{0.01}5d^{9.96}6p^{0.01}6d^{0.02}$

Ne: $[\text{core}]2s^{1.99}2p^{5.95}3s^{0.01}3p^{0.04}$

Au^+-Ar: Au: $[\text{core}]6s^{0.08}5d^{9.94}6p^{0.02}6d^{0.03}$

Ar: $[\text{core}]3s^{1.99}3p^{5.92}4p^{0.02}$

Au^+-Kr: Au: $[\text{core}]6s^{0.14}5d^{9.93}6p^{0.03}6d^{0.03}$

Kr: $[\text{core}]4s^{1.99}4p^{5.87}5p^{0.02}$

Au^+-Xe: Au: $[\text{core}]6s^{0.23}5d^{9.92}6p^{0.04}6d^{0.03}$

Xe: $[\text{core}]5s^{1.98}5p^{5.79}6p^{0.01}$

These analyses, together with the partial charges, gives clear evidence that there is significant sharing of electron density between the gold and rare gas centers for Rg = Kr and Xe, and thus that chemical bonding is occurring; although there is some evidence of small amounts of charge transfer in the two lighter systems, the evidence is clearest for the two heavier species. The main mode of density transfer is from a filled pσ orbital on the rare gas, and into the LUMO, the 6sσ orbital on the metal center, completely in line with deductions made by Pyykkö.[21,23,42] Interestingly, there is evidence of a small amount of reduced electron density in the $5d_{z^2}\sigma$ orbital of Au^+, which is <0.1 e but increases monotonically from Au^+-Ne to Au^+-Xe – this might be due to a small amount of back-bonding, but the effect is so small that other factors could be playing a role.

TABLE 4: Comparison of Au–Xe Bond Distances and Bond Strengths

species	bond distance/Å	bond strength/cm^{-1}
Au^+-Xe[a]	2.60	10,529
$(F_3As)Au^+$-Xe[b]	2.61	11,450
$Au^{2+}-Xe_4$[c]	2.74 ± 0.01	
cis-$Au^{2+}(Xe)_2$[c]	2.66	
	2.67	
trans-$Au^{2+}(Xe)_2$[c]	2.71	
trans-$(F^-)(SbF_5^-)Au^{3+}(Xe)_2$[d]	2.59	
	2.62	

[a] Present work. [b] Reference 3. [c] Reference 2. [d] Reference 4.

III. Discussion

From the above model-potential analyses, and the NBO analyses of charge distributions, we conclude that Au^+-Ne can be described as a physically bound complex, with higher-order terms in R^{-6}, R^{-7}, R^{-8}, etc. definitely being required to rationalize the bonding. Thus, dispersion terms (R^{-6}, R^{-8}) for example play an important role in the bonding of Ne to Au^+, because of the moderate polarizability of the $Au^+(5d^{10})$ outer shell of electrons. This is in contrast to the alkali-metal ion/Ne complexes, where the leading ion-induced dipole R^{-4} terms dominate. For example, Na^+-Ne[19] has almost as high a D_e value, 514 cm^{-1}, as that of Au^+-Ne, 619 cm^{-1}, but at a lower R_e value, 2.47 Å, *versus* 2.692 Å for Au^+-Ne. However, in contrast to Au^+-Ne, where the calculated Z value drops from 1.40 to 1.08 when the R^{-6}, R^{-7} and R^{-8} terms in eq 1 are added to the R^{-4} term, the Z value for Na^+-Ne only drops from 1.11 to 1.02. This is similar to the cases[7] of Mg^+-Ar *versus* Na^+-Ar, where the R_e and D_e values are both quite similar, but for Na^+-Ar, the R^{-4} term contributes 71% of the bonding energy, and for Mg^+-Ar, the R^{-4} term contributes only 41%, mostly because of the large dispersion terms.

In contrast, for Au^+-Ar, Au^+-Kr and Au^+-Xe, the calculated Z values and NBO analyses show an increasing amount of chemical contributions, and for the latter two, certainly beyond what can be rationalized by eq 1 only. As can be seen from the above, the Au^+-Xe and Au^+-Kr covalent contributions result for the most part from donation of pσ electron density on the Rg atom to the empty, low-lying $Au^+(6s)$ orbital. As has been discussed before by others,[23] the $Au^+(6s)$ orbital is stabilized by *ca.* 2 eV by large relativistic effects. Because of this, and because the $5d^{10}$ outer shell of Au^+ is small, owing to the lanthanide contraction (reducing interatomic repulsion) Au^+ forms particularly strong coordinate covalent bonds with other ligands,[23] such as H_2O, NH_3, and C_2H_4; in fact, the $Au^+-C_2H_4$ bond is stronger than that of any transition-metal $M^+-C_2H_4$ bond.

Shown in Table 4 is a comparison of the bonding of the Au^+-Xe diatomic gas-phase ion, with $Au^{n+}-Xe$ (n = 1, 2 and 3) solid-state ions. Both the bond distance and calculated bond strength for the Au^+-Xe bond in the $(F_3As)Au^+(Xe)$ complex are remarkably similar to those of the gas-phase Au^+-Xe diatomic ion, apparently indicating that the weakly bound F_3-As ligand has very little effect on the Au^+-Xe bond. Surprisingly, the Au^+-Xe bonds in *trans*-$(F^-)(SbF_5^-)Au^{3+}(Xe)_2$ also have bond lengths essentially the same as the "free" Au^+-Xe

ion. This may indicate that although the gold atom formally has oxidation state III, the actual charge on the gold ion is closer to 1.0, owing to strong charge donation to the gold center by the two negatively charged ligands, F^- and SbF_5^-. It is also possible that the effective charge on the Au(III) center is somewhere between +1 and +3, but that the repulsion with the two large negative ligands is greater than in the "free" *trans*-$Au^{3+}(Xe)_2$ ion.

The bond distance in the $Au^{2+}(Xe)_4$ square-planar ion[2] is substantially *larger* (2.74 Å) than in the Au^+-Xe free ion, which is also surprising. However, an examination of crystallographic data shows that the Xe−Xe diatomic distances can be calculated to be 3.88 Å, even lower than the Xe−Xe "hard-sphere" distance[7] (the distance at which the interatomic potential energy is zero) of 4.1 Å. This indicates that there is Xe−Xe repulsion (steric hindrance) in the square-planar complex, so that the Xe atoms cannot approach the Au^{2+} ions even as closely as in the "free" Au^+-Xe ion. (The bond distance of the van der Waals' Xe−Xe diatomic bond is 4.36 Å.)[7]

The *cis*- and *trans*-$Au^{2+}(Xe)_2$ complexes are in pseudo-square-planar structures, with two F atoms of the Sb-containing counterions occupying the third and fourth sites. The fact that the $Au^{2+}(Xe)$ bonds are slightly shorter than those in $Au^{2+}(Xe)_4$ may reflect the fact that there is either no (in the case of *trans*) or somewhat less (in the case of *cis*) steric hindrance.

It is interesting to note that although several Au(I, II, III) complexes of Xe have now been prepared, similar complexes of Kr have not been reported, even though their synthesis has been attempted.[4] The free Au^+-Kr ion is less bound than the free Au^+-Xe ion but still shows definite signs of covalent interactions. However, most of the solid-state Xe complexes have been made[2−4] by displacement of even more weakly bound ligands, such as AsF_3, and it is possible that the Au−Kr bond is just not sufficiently strong for such displacement to occur. In contrast, $M(CO)_5Kr$ complexes (M = Cr, Mo and W) have been observed[43] as transients in the photolysis of $M(CO)_6$ complexes in excess inert gas. In this case, ligand displacement is not required, and Rg atoms can complex directly to the empty $M(CO)_5$ coordination site. Other Kr-containing species have also been seen in the Poliakoff and George groups (see, for example, ref 44).

IV. Conclusions

It is concluded from model-potential and NBO analyses of the charge distributions in the Au^+-Rg complexes (Rg = Ne, Ar, Kr and Xe) that physical interaction is sufficient to explain the bonding in Au^+-Ne but that increasingly larger amounts of covalent bonding are required to explain the larger bond energies along the series Au^+-Ar, Au^+-Kr and Au^+-Xe. For Au^+-Kr and Au^+-Xe, both the model potential analysis and the NBO results indicate that a partial chemical bond is formed. For Au^+-Ar, although the model potential analysis yields a Z value >1.2, the effect of higher-order terms may bring this below 1.1; on the other hand, the NBO analysis indicates only a small sharing of electron density between the Au^+ and Ar. For Au^+-Ne, there is no strong evidence of chemical bonding. Our results are quite consistent with those of Pyykkö and co-workers, who suggested that the particularly strong bonding in Au^+-Xe diatomic ion could have a major chemical component,[21,23] but negate those of ref 22 who suggest the interaction is wholly physical, even for Au^+-Xe.

It would be desirable to have experimental measurements of the bond distances and bond strengths of all of the Au^+-Rg complexes to compare with the very high level *ab initio* calculated values reported in the present work. We are currently attempting experiments that we hope will lead to accurate determinations of such values.

Added Note

Very recently, as part of a study to examine the bonding in RgAuF complexes, Belpassi et al.[45] have also looked at Au^+-Rg (Rg = Ar−Xe) complexes employing triple-ζ quality all-electron basis sets and a relativistic CCSD(T) method, as well as employing a DFT method. Their relativistic CCSD(T) results for the spectroscopic constants (R_e, D_e, ω_e and k) are very similar to those reported herein. In addition, their calculated charges on the Rg atom have a very similar trend to the ones we report, although theirs are a little higher. Overall then, the two studies agree that there are emergent chemical bonds in the heavier Au^+-Rg species, although the means of determining this are quite distinct.

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