Covalency in ArAu$^+$ and Related Species?

J. P. Read* and A. D. Buckingham

Contribution from the University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW UK

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Abstract: The interaction between a spherical metal ion M$^+$ and a rare gas atom Rg is analyzed in terms of the long-range effects of polarization and dispersion. The inclusion of higher-order linear polarization effects is found to enhance significantly the polarization contribution to binding compared to a simple charge-induced dipole interaction. The discrepancy between experimental or *ab initio* binding energies and the long-range energy of polarization and dispersion is found to be much reduced when higher-order effects are included, indicating a negligible role for covalency in these ions.

Introduction

Chemical bonds between metal ions and rare gas atoms have been detected experimentally and their existence predicted by *ab initio* computation.[1-4] Recent calculations at levels up to CCSD(T) predict the existence of diatomic species of the form RgAu$^+$, with binding energies of up to 0.9 *e*V for XeAu$^+$;[5] similar stabilities have been reported for the RgCu$^+$ analogues.[1,3]

The binding energies of the RgAu$^+$ species increase in passing from He to Xe, mirroring the increase in the dipole polarizability, α_1, of the Rg atoms. This has been interpreted[5] in terms of the R^{-4} interaction between the charge q on the metal ion and the induced dipole on the Rg:

$$U_D(R) = -\frac{q^2\alpha_1}{2R^4} \qquad (1)$$

where R is the internuclear separation of M$^+$ and Rg.

Equation 1, which is complete in the asymptotic limit as $R \to \infty$, accounts for about 50% of the calculated binding energy of XeAu$^+$;[5] the remainder of the interaction is ascribed to covalent effects and taken as evidence for significant covalency in the Xe−Au$^+$ bond.[5] The R^{-4} interaction of eq 1, however, omits the induction of higher multipole moments on either M$^+$ or Rg. These higher-order terms vary as R^{-n} where $n > 4$, and so may become significant at smaller R, particularly around R_e. To complete the long-range view of bonding in these diatomics, the dispersion energy, the leading term of which varies as R^{-6}, may be estimated.[6] The inclusion of higher order polarization effects and the dispersion energy significantly enhances the long-range contribution to the RgM$^+$ interaction, thereby reducing the inferred degree of covalency.

Theory

Let a spherical ion M$^+$, such as the $^1S_0$ ground state of Au$^+$ or Cu$^+$, be located at the origin of the coordinate system, with a rare gas atom a distance R along the z axis. Considering only linear polarization,

and with no charge transfer between the metal ion and rare gas atom, the interaction may be written[6,7]

$$U_{pol}(R) = \frac{1}{2}\sum_{n=1}^{N^{Rg}} \frac{\xi_n^{Rg}}{n!}\frac{\partial V_{Rg}^{(0)}}{\partial z^n} \qquad (2)$$

where N^{Rg} is the maximum order of multipole induced upon the Rg atom, ξ_n^{Rg} the nth order induced multipole on Rg, and $V_{Rg}^{(0)}$ the potential at the Rg site due to the permanent moments of the cation.

Equation 2 may be developed further by noting that the potential at a point (r, θ) due to an axisymmetric set of multipoles $\{\xi_n\}$ at the origin is

$$V(r, \theta) = \sum_{n=0}^{N} \frac{\xi_n P_n(\cos\theta)}{r^{n+1}} \qquad (3)$$

and the mth derivative with respect to z may be written

$$\frac{\partial^m V}{\partial z^m} = (-1)^m \sum_{n=0}^{N} \frac{\xi_n P_{n+m}(\cos\theta)(n+m)!}{n!r^{n+m+1}} \qquad (4)$$

where $P_n(\cos\theta)$ is the nth Legendre polynomial.[8]

Since we assume no charge transfer between the metal ion and the rare gas atom, the only permanent moment is the charge $q = \xi_0^{M^+}$ of the spherical M$^+$, and eq 2 may be rewritten

$$U_{pol}(R) = \frac{q}{2}\sum_{n=1}^{N^{Rg}} \frac{(-1)^n \xi_n^{Rg}}{R^{n+1}} \qquad (5)$$

Equation 5 allows the linear polarization interaction to be described to arbitrarily high order if the induced moments of the Rg atom are known.

The induced moments may be written in terms of the multipolar polarizabilities. Restricting the analysis to linear effects, the nth order induced moment is proportional to the $(n-1)$th derivative of the electric field E_z:

$$\xi_n = \alpha_n E_{zz...z}^{(n-1)} = -\alpha_n \frac{\partial^n V}{\partial z^n} \qquad (6)$$

where α_n is the nth order multipolar polarizability: α_1 is the dipole polarizability, and α_2 and α_3 are the quadrupole and octopole polarizabilities respectively.[9] Values for α_1 are available from experiment or calculation; *ab initio* calculations of the quadrupole and octopole polarizabilities of the rare gases have been performed.[10,11] Since the

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(8) Abramowicz, M.; Stegun, I. A., Eds. *Handbook of Mathematical Functions*, 1st ed.; Dover, NY, 1965.

(9) Note that the nth order polarizability is sometimes defined to be $n!$ times that of eq 6: Dalgarno, A. *Adv. Phys.* **1962**, *11*, 281.

induced moments depend on the total potential derivative arising from the permanent and induced moments of the other species, the polarization energy is determined by the solution of $N^{M^+} + N^{Rg}$ simultaneous equations. This procedure corresponds to the linear induction energy iterated to infinite order.

We shall limit the multipolar polarizabilities α_n to $N^{M^+} = 1$ for M^+ and $N^{Rg} = 3$ for Rg. Curtailing the induced multipoles at these levels gives a polarization energy

$$U_{DQO,D}(R) = -\frac{q^2}{2R^4} \times$$
$$\frac{\alpha_1^{Rg} + \frac{2\alpha_2^{Rg}}{R^2} + \frac{6\alpha_3^{Rg}}{R^4} - 2\alpha_1^{M^+}\left(\frac{\alpha_1^{Rg}\alpha_2^{Rg}}{R^8} + \frac{12\alpha_1^{Rg}\alpha_3^{Rg}}{R^{10}} + \frac{6\alpha_2^{Rg}\alpha_3^{Rg}}{R^{12}}\right)}{1 - \frac{2\alpha_1^{M^+}}{R^6}\left(2\alpha_1^{Rg} + \frac{9\alpha_2^{Rg}}{R^2} + \frac{48\alpha_3^{Rg}}{R^4}\right)} \tag{7}$$

where the subscript DQO,D indicates the inclusion of dipole, quadrupole, and octopole polarizabilities on the Rg atom and the dipole polarizability alone on the M^+ cation. Successively lower-order approximations to the polarization energy may be obtained by setting the appropriate α_n to zero in eq 7. Retaining only α_1^{Rg} gives the asymptotic result of eq 1. If we take $\alpha_1^{M^+} = 0$ we obtain the result for a point charge q interacting with the rare gas atom. The iterated linear induction energy of eq 7 diverges at short range as the denominator approaches zero, but we note that the incipient divergence at distances greater than this does not invalidate a "long-range" description of complexes of this type, because of the smallness of the polarizabilities utilized.[12] At $R \simeq R_e$, the higher-order terms in eq 7 may contribute significantly to the interaction energy. For XeAu+ and ArAu+, the R_e calculated at the CCSD(T) level are 2.761 and 2.730 Å, respectively.[5]

The leading nonlinear polarization contributions to binding are described by the dipole−quadrupole hyperpolarizability B and second hyperpolarizability γ of the Rg species.[6] Neglecting iteration of the nonlinear induced moments gives

$$U_{DQOB\gamma,D}(R) = U_{DQO,D}(R) + \frac{q^3 B}{2R^7} - \frac{q^4\gamma}{24R^8} \tag{8}$$

The term involving the dipole−quadrupole hyperpolarizability B varies as R^{-7} and constitutes the dominant nonlinear effect.

To complete the long-range view of binding in the RgM+ complexes, the effect of dispersion must be estimated. The sum over states in the formulation of the dispersion energy may be approximated by utilizing the first ionization energies of the two species.[6,13] Including linear effects up to the fluctuating octopole on the Rg and the fluctutating dipole on M^+ as in eq 7 gives

$$U_{disp}(R) = -\frac{3U_{M^+}U_{Rg}}{2(U_{M^+} + U_{Rg})}\alpha_1^{M^+}\left[\frac{\alpha_1^{Rg}}{R^6} + \frac{5\alpha_2^{Rg}}{R^8} + \frac{28\alpha_3^{Rg}}{R^{10}} + ...\right] \tag{9}$$

where U_{M^+} and U_{Rg} are the first ionization energies of the M^+ ion and Rg atom. The quadrupole and octopole polarizabilities of M^+ would increase the magnitude of the dipersion energy.

Discussion

Figure 1 shows the polarization contribution to the interaction energy of eqs 7 and 8 as a function of internuclear separation R. The static dipole polarizability of Au+ is $\alpha_1 = 11.6(4\pi\epsilon_0)\cdot a_0^3$,[14] and the static multipolar polarizabilities of Ar are $\alpha_1 = 11.08(4\pi\epsilon_0)a_0^3$, $\alpha_2 = 25.93(4\pi\epsilon_0)a_0^5$, and $\alpha_3 = 89.40(4\pi\epsilon_0)\cdot$

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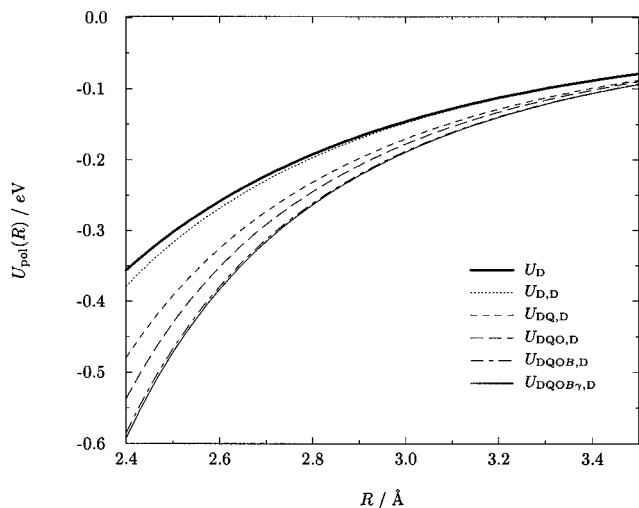(15) Kumar, A.; Meath, W. J. *Can. J. Chem.* **1985**, *63*, 1616.

Figure 1. Polarization contributions to the binding of ArAu+ as a function of internuclear separation R. The subscripts D, Q, and O indicate the inclusion of dipole, quadrupole, and octopole polarizabilities, respectively; B and γ are the dipole−quadrupole and second hyperpolarizabilities. The first set of subscripts indicate those properties of the inert gas atom which were included in the calculation, the second set those of the Au+ ion. $U_D(R)$ is the expression previously compared against to infer covalency within the complex[5] ($R_e = 2.730$ Å).
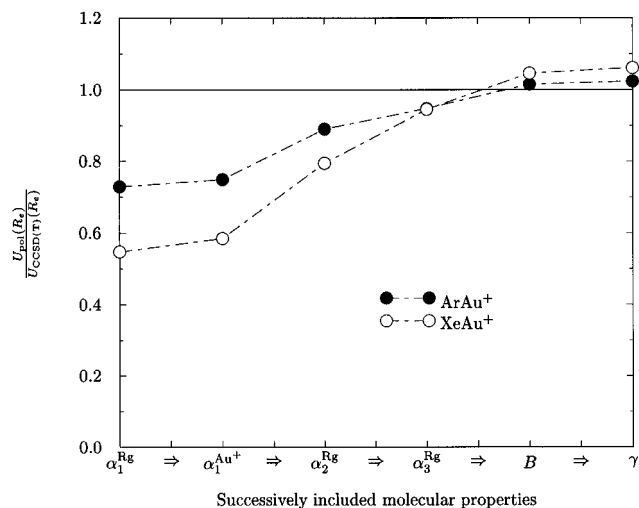

Figure 2. Convergence of the polarization contribution to the binding of ArAu+ and XeAu+ at $R = R_e$. The leftmost result is the expression previously compared against to infer covalency within the complex[5] ($R_e^{ArAu^+} = 2.730$ Å and $R_e^{XeAu^+} = 2.761$ Å).

a_0^7.[10,15] The dipole−quadrupole and second hyperpolarizabilities of Ar are $B = -139.9(4\pi\epsilon_0)^2 e^{-1} a_0^6$ and $\gamma = 1166(4\pi\epsilon_0)^3 e^{-2} a_0^7$, respectively.[16,17]

The results in Figure 1 indicate that the inclusion of higher-order linear polarization effects significantly enhances the polarization contribution to the binding energy of ArAu+. As $R \to \infty$, the polarization models all tend to the asymptotic form of eq 1. The effect of each polarizability on the polarization energy when $R = R_e$ can be seen in Figure 2. The inclusion of the dipole polarizability of Au+ strengthens the interaction by only 3% compared to the asymptotic result of eq 1; the more important effect is the inclusion of the higher-order linear polarizabilities of the rare gas atom. $U_{DQO,D}(R_e)$ provides about 95% of the calculated $D_e = 0.292$ eV, compared to 73% for the charge-induced dipole interaction of eq 1. The inclusion

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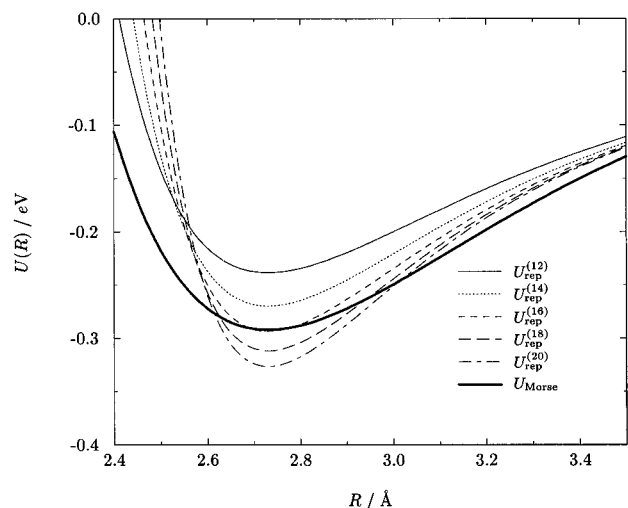(17) Shelton, D. P. *Phys. Rev. A* **1990**, *42*, 2578.

Figure 3. The potential energy surface for the interaction between Ar and Au$^+$, where R is the internuclear separation. The attractive contributions to binding are taken to be $U_{DQOB\gamma,D}(R)$ and $U_{disp}(R)$ of eqs 8 and 9, and an empirical repulsion $U_{rep}^{(n)}(R) = C_n R^{-n}$ is fitted with C_n determined by requiring that the position of the minimum agrees with that determined by CCSD(T) calculation.[5] $U_{Morse}(R)$ is a Morse potential fit to CCSD(T) results with parameters $R_e = 2.730$ Å, $D_e = 0.292$ eV, and $\nu = 123$ cm^{-1}.[5]
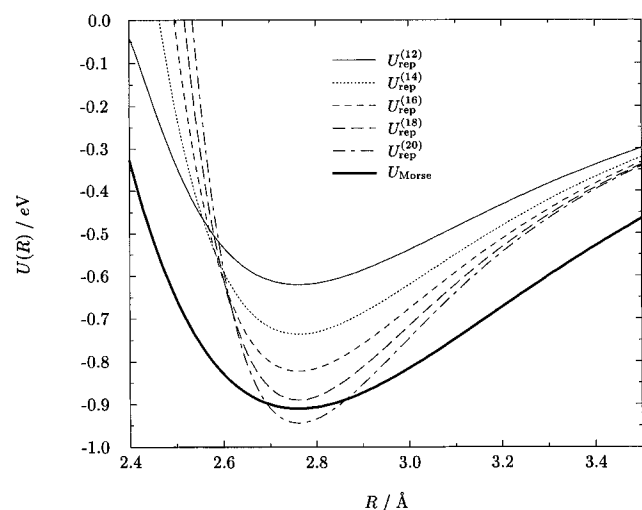

Figure 4. The potential energy surface for the interaction between Xe and Au+, where R is the internuclear separation. The attractive contributions to binding are taken to be $U_{DQOB\gamma,D}(R)$ and $U_{disp}(R)$ of eqs 8 and 9, and an empirical repulsion $U_{rep}^{(n)}(R) = C_n R^{-n}$ is fitted with C_n determined by requiring that the position of the minimum agrees with that determined by CCSD(T) calculation.[5] $U_{Morse}(R)$ is a Morse potential fit to CCSD(T) results with parameters $R_e = 2.761$ Å, $D_e = 0.910$ eV, and $\nu = 129$ cm^{-1}.[5]

of nonlinear effects through the hyperpolarizabilities B and γ by using eq 8 enhances the induction contribution to binding by another 10%, with 9% of that enhancement coming from the longer-range contribution of the dipole–quadrupole hyperpolarizability B: the relative importance of the nonlinear terms will be greater in complexes where the ion is more highly charged. $U_{disp}(R_e)$ provides a further 55% of the calculated D_e, leaving the repulsion energy to contribute -57% of D_e. XeAu$^+$ shows a similar trend, although the convergence with respect to the addition of linear multipolar polarizabilities is less complete (see Figure 2).

Figure 3 shows the potential energy surface for the interaction between Au$^+$ and Ar as a function of separation R; Figure 4 shows the analogous result for the XeAu$^+$ complex. The
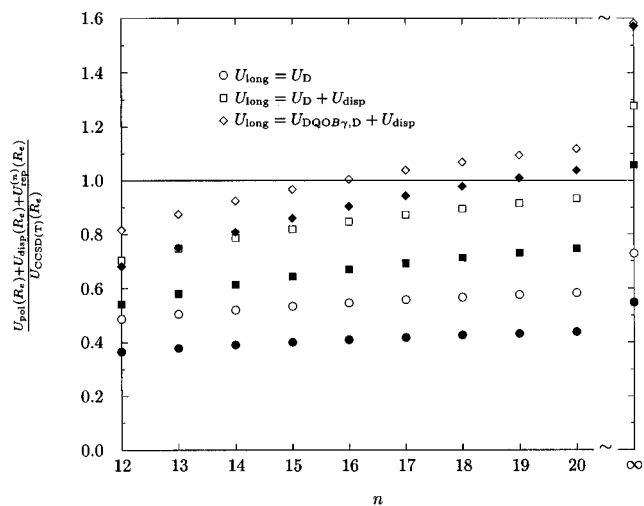

Figure 5. The ratio of the sum of the long-range interaction energies of eqs 7–9 and a repulsive potential of the form $U_{rep}^{(n)}(R) = C_n R^{-n}$ at $R = R_e$ to the *ab initio* CCSD(T) result[5] for various integer choices of n. Open symbols refer to ArAu$^+$; filled symbols refer to XeAu$^+$.

polarizabilities of Xe used in the calculations are $\alpha_1 = 27.16\cdot(4\pi\epsilon_0)a_0^3$, $\alpha_2 = 111.6(4\pi\epsilon_0)a_0^5$, $\alpha_3 = 606.8(4\pi\epsilon_0)a_0^7$, $B = -708.9(4\pi\epsilon_0)^2 e^{-1}a_0^6$, and $\gamma = 6882(4\pi\epsilon_0)^3 e^{-2}a_0^7$;[10,15–17] the ionization energies of the species are $U_{Au^+} = 20.5$ eV, $U_{Ar} = 15.759$ eV, and $U_{Xe} = 12.130$ eV.[18] The attractive contribution to binding is taken to be the sum of the induction and dispersion energies of eqs 8 and 9, and an empirical repulsive term of the form

$$U_{rep}^{(n)}(R) = C_n/R^n \tag{10}$$

is assumed, with the parameter C_n determined by requiring that the position of the minimum of the potential energy curve agree with the result of CCSD(T) calculation.[5] Increasing the value of n is seen to augment the well depth of the potential curve, with best agreement with the *ab initio* D_e for ArAu$^+$ being achieved for $n = 16$. Agreement for XeAu$^+$ can be achieved only with a higher choice of n giving a repulsive potential which appears unphysically steep. This stems from yet higher-order attractive contributions to binding which have been neglected in the formulation of eqs 8 and 9—these may be inferred from the poorer convergence with respect to the addition of linear multipolar polarizabilities of the polarization energy of XeAu$^+$ compared to ArAu$^+$, shown in Figure 2—and uncertainties in the calculated values of the higher polarizabilities and hyperpolarizabilities. We note that, especially for XeAu$^+$, the Morse curve taken from CCSD(T) calculation seems to overestimate binding at large R; the mathematical form of the Morse potential prevents it from tending to the correct asymptotic form of eq 1, and vibrational frequencies derived from it will correspondingly be underestimated.

Irrespective of the choice of repulsive potential, the inclusion of higher-order linear and nonlinear polarization effects, and the dispersion energy, significantly reduces the inferred degree of covalency of the RgAu$^+$ complexes. This can be seen in Figure 5 in which the fractions of the calculated binding energy recovered by various models of the long-range energy are compared for each n in eq 10. For every choice of n the conclusion is unchanged: the charge-induced dipole interaction of eq 1 should not be used as a basis for the inference of covalency in these types of complex. It neglects induction and

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dispersion effects which make up approximately 40% of the binding energy, and the degree of covalency is consequently overestimated by the same amount.

Conclusion

The calculated binding energies of the RgAu$^+$ species may be explained in terms of long-range polarization and dispersion interactions, with the dominant attractive term in the potential coming from the polarization of Rg by M$^+$. The largest contributor to the induction energy is the charge-induced dipole interaction of eq 1, but higher-order effects are significant near the equilibrium bond length. The discrepancy between eq 1 and the calculated D_e can thus be explained without recourse to large covalent interaction, but rather in terms of the neglect of the induced dipole on Au$^+$, significant higher induced moments on Rg, and the dispersion interaction. The need to invoke covalency within the RgAu$^+$ bond appears to be unproven, even for diffuse species such as Xe.

Though applied to Au$^+$ complexes, the results are readily applicable to other spherical ions, and may be used to interpret and predict the binding energy of complexes of these ions with rare gas atoms. Those M$^+$ with electron affinities less than the ionization energy of Xe, such as Cu$^+$ or Ag$^+$ (with electron affinities of 7.726 and 7.576 eV, respectively[18]), are expected to be similar to Au$^+$ in XeAu$^+$, with the interaction dominated by long-range effects; those with electron affinities in excess of the ionization energy of Xe, such as Hg^{2+} or Tl^{3+}, are expected to show appreciable covalency. Ca^{2+}, with an electron affinity of 11.871 eV,[18] only just less than the ionization energy of Xe, provides an intermediate example in which the contributions to D_e from covalent and long-range effects may both be significant.