

# Covalency in $\text{ArAu}^+$ and related species?

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## Abstract

The interaction between a spherical metal ion  $\text{M}^+$  and a rare gas atom Rg is analysed in terms of the long-range effects of polarisation and dispersion. The inclusion of higher-order linear polarisation effects is found to enhance significantly the polarisation 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 polarisation and dispersion is found to be significantly 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.<sup>1-4</sup> Recent calculations at levels up to CCSD(T) predict the existence of diatomic species of the form  $\text{RgAu}^+$ , with binding energies of up to 0.9 eV for  $\text{XeAu}^+$ ;<sup>5</sup>

similar stabilities have been reported for the  $\text{RgCu}^+$  analogues.<sup>1,3</sup>

The binding energies of the  $\text{RgAu}^+$  species increase in passing from He to Xe, mirroring the increase in the dipole polarisability,  $\alpha_1$ , of the Rg atoms. This has been interpreted<sup>5</sup> in terms of the  $R^{-4}$  interaction between the charge  $q$  on the metal ion and the induced dipole on the Rg:

$$U_{\text{D}}(R) = -\frac{q^2 \alpha_1}{2R^4} \quad (1)$$

where  $R$  is the internuclear separation of  $\text{M}^+$  and Rg.

Eq. (1), which is complete in the asymptotic limit as  $R \rightarrow \infty$ , accounts for about 50% of the calculated binding energy of  $\text{XeAu}^+$ :<sup>5</sup> the remainder of the interaction is ascribed to covalent effects and taken as evidence for significant covalency in the Xe—Au<sup>+</sup> bond.<sup>5</sup> The  $R^{-4}$  interaction of Eq. (1), however, omits the induction of higher multipole moments on either  $\text{M}^+$  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.<sup>6</sup> The inclusion of higher order polarisation effects and the dispersion energy significantly enhances the long-range contribution to the  $\text{RgM}^+$  interaction, thereby reducing the inferred degree of covalency.

## Theory

Let a spherical ion  $\text{M}^+$ , such as the  $^1\text{S}_0$  ground state of  $\text{Au}^+$  or  $\text{Cu}^+$ , be located at the origin of the coordinate system, with a rare gas atom a distance  $R$  along the  $z$  axis. Considering only linear polarisation, and with no charge transfer between metal ion and rare gas atom, the interaction may be written<sup>6,7</sup>

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

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

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

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

and the  $m$ th derivative with respect to  $z$  may be written

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

where  $P_n(\cos \theta)$  is the  $n$ th Legendre polynomial.<sup>8</sup>

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

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

Eq. (5) allows the linear polarisation 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 polarisabilities. Restricting the analysis to linear effects, the  $n$ th order induced moment is proportional to the  $(n-1)$ th derivative of the electric field  $E_z$ :

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

where  $\alpha_n$  is the  $n$ th order multipolar polarisability:  $\alpha_1$  is the dipole polarisability,  $\alpha_2$  and  $\alpha_3$  the quadrupole and octopole polarisabilities respectively. <sup>†</sup> Values for  $\alpha_1$  are available from experiment or calculation; *ab initio* calculations of the quadrupole and octopole polarisabilities of the rare gases have been performed.<sup>10,11</sup> Since the induced moments depend on the total potential derivative arising from the permanent and induced moments of the other species, the polarisation energy is determined by the solution of  $N^{\text{M}^+} + N^{\text{Rg}}$  simultaneous equations. This procedure corresponds to the linear induction energy iterated to infinite order.

We shall limit the multipolar polarisabilities  $\alpha_n$  to  $N^{\text{M}^+} = 1$  for  $\text{M}^+$  and  $N^{\text{Rg}} = 3$  for Rg. Curtailing the induced multipoles at these levels gives a polarisation energy

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

where the subscript DQO,D indicates the inclusion of dipole, quadrupole and octopole polarisabilities on the Rg atom and the dipole polarisability alone on the  $\text{M}^+$  cation. Successively lower-order approximations to the polarisation energy may be obtained by setting the appropriate  $\alpha_n$  to zero in Eq. (7). Retaining only  $\alpha_1^{\text{Rg}}$  gives the asymptotic result of Eq. (1). If we take  $\alpha_1^{\text{M}^+} = 0$  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 appears less pronounced for small polyatomic complexes when single-site, rather than distributed, polarisabilities are utilised.<sup>12</sup> At  $R \simeq R_e$ , the higher-order terms in Eq. (7) may contribute significantly to the interaction energy. For  $\text{XeAu}^+$  and  $\text{ArAu}^+$ , the  $R_e$  calculated at the CCSD(T) level are 2.761 Å and 2.730 Å respectively.<sup>5</sup>

The leading non-linear polarisation contributions to binding are described by the dipole-quadrupole hyperpolarisability  $B$  and second hyperpolarisability  $\gamma$  of the Rg species.<sup>6</sup> Neglecting iteration of the non-linear induced moments gives

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<sup>†</sup>Note that the  $n$ th order polarisability is sometimes defined to be  $n!$  times that of Eq. (6).<sup>9</sup>

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

The term involving the dipole-quadrupole hyperpolarisability  $B$  varies as  $R^{-7}$  and constitutes the dominant non-linear effect.

To complete the long-range view of binding in the  $\text{RgM}^+$  complexes, the effect of dispersion must be estimated. The sum over states in the formulation of the dispersion energy may be approximated by utilising the first ionisation energies of the two species.<sup>6,13</sup> Including linear effects up to the fluctuating octopole on the Rg and the fluctuating dipole on  $\text{M}^+$  as in Eq. (7) gives

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

where  $U_{\text{M}^+}$  and  $U_{\text{Rg}}$  are the first ionisation energies of the  $\text{M}^+$  ion and Rg atom. The quadrupole and octopole polarisabilities of  $\text{M}^+$  would increase the magnitude of the dispersion energy.

## Discussion

Figure 1 shows the polarisation contribution to the interaction energy of Eqs. (7–8) as a function of internuclear separation  $R$ . The static dipole polarisability of  $\text{Au}^+$  is  $\alpha_1 = 11.6 \, 4\pi\epsilon_0 a_0^3$ ,<sup>14</sup> and the static multipolar polarisabilities 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  $\alpha_3 = 89.40 \, 4\pi\epsilon_0 a_0^7$ .<sup>10,15</sup> The dipole-quadrupole and second hyperpolarisabilities 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.<sup>16,17</sup>

The results in Figure 1 indicate that the inclusion of higher-order linear polarisation effects significantly enhances the polarisation contribution to the binding energy of  $\text{ArAu}^+$ . As  $R \rightarrow \infty$ , the polarisation models all tend to the asymptotic form of Eq. (1). The effect of each polarisability on the polarisation energy when  $R = R_e$  can be seen in Figure 2. The inclusion of the dipole polarisability of  $\text{Au}^+$  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 polarisabilities of the rare gas atom.  $U_{\text{DQO,D}}(R_e)$  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 of non-linear effects through the hyperpolarisabilities  $B$  and  $\gamma$  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 hyperpolarisability  $B$ : the relative importance of the non-linear terms will be greater in complexes where the ion is more highly charged.  $U_{\text{disp}}(R_e)$  provides a further 55% of the calculated  $D_e$ , leaving the repulsion energy to contribute -57% of  $D_e$ .  $\text{XeAu}^+$  shows a similar trend, although the convergence with respect to the addition of linear multipolar polarisabilities is less complete (see Figure 2).

Figure 3 shows the potential energy surface for the interaction between  $\text{Au}^+$  and Ar as a function of separation  $R$ ; Figure 4 shows the analogous result for the  $\text{XeAu}^+$  complex. The polarisabilities of Xe used in the calculations are  $\alpha_1 = 27.16 \ 4\pi\epsilon_0 a_0^3$ ,  $\alpha_2 = 111.6 \ 4\pi\epsilon_0 a_0^5$ ,  $\alpha_3 = 606.8 \ 4\pi\epsilon_0 a_0^7$ ,  $B = -708.9 \ (4\pi\epsilon_0)^2 e^{-1} a_0^6$ , and  $\gamma = 6882 \ (4\pi\epsilon_0)^3 e^{-2} a_0^{7,10,15-17}$  the ionisation energies of the species are  $U_{\text{Au}^+} = 20.5$  eV,  $U_{\text{Ar}} = 15.759$  eV, and  $U_{\text{Xe}} = 12.130$  eV.<sup>18</sup> 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

$$U_{\text{rep}}^{(n)}(R) = \frac{C_n}{R^n} \quad (10)$$

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.<sup>5</sup> 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  $\text{ArAu}^+$  being achieved for  $n = 16$ . Agreement for  $\text{XeAu}^+$  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. (8–9) — these may be inferred from the poorer convergence with respect to the addition of linear mutlipolar polarisabilities of the polarisation

energy of  $\text{XeAu}^+$  compared to  $\text{ArAu}^+$ , shown in Figure 2 — and uncertainties in the calculated values of the higher polarisabilities and hyperpolarisabilities. We note that, especially for  $\text{XeAu}^+$ , 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 non-linear polarisation effects, and the dispersion energy, significantly reduces the inferred degree of covalency of the  $\text{RgAu}^+$  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 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  $\text{RgAu}^+$  species may be explained in terms of long-range polarisation and dispersion interactions, with the dominant attractive term in the potential coming from the polarisation of Rg by  $\text{M}^+$ . 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  $\text{Au}^+$ , significant higher induced moments on Rg, and the dispersion interaction. The need to invoke covalency within the  $\text{RgAu}^+$  bond appears to be unproven, even for diffuse species such as Xe.

Though applied to  $\text{Au}^+$  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  $\text{M}^+$

with electron affinities less than the ionisation energy of Xe, such as  $\text{Cu}^+$  or  $\text{Ag}^+$  (with electron affinities of 7.726 and 7.576 eV respectively<sup>18</sup>), are expected to be similar to  $\text{Au}^+$  in  $\text{XeAu}^+$ , with the interaction dominated by long-range effects; those with electron affinities in excess of the ionisation energy of Xe, such as  $\text{Hg}^{2+}$  or  $\text{Tl}^{3+}$ , are expected to show appreciable covalency.  $\text{Ca}^{2+}$ , with an electron affinity of 11.871 eV,<sup>18</sup> only just less than the ionisation energy of Xe, provides an intermediate example in which the contributions to  $D_e$  from covalent and long-range effects may both be significant.

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## Figure Captions

**Figure 1:** Polarisation contributions to the binding of  $\text{ArAu}^+$  as a function of internuclear separation  $R$ . The subscripts D,Q, and O indicate the inclusion of dipole, quadrupole and octopole polarisabilities respectively;  $B$  and  $\gamma$  are the dipole-quadrupole and second hyperpolarisabilities. 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  $\text{Au}^+$  ion.  $U_D(R)$  is the expression previously compared against to infer covalency within the complex.<sup>5</sup> ( $R_e = 2.730 \text{ \AA}$ ).

**Figure 2:** Convergence of the polarisation contribution to the binding of  $\text{ArAu}^+$  and  $\text{XeAu}^+$  at  $R = R_e$ . The leftmost result is the expression previously compared against to infer covalency within the complex.<sup>5</sup> ( $R_e^{\text{ArAu}^+} = 2.730 \text{ \AA}$  and  $R_e^{\text{XeAu}^+} = 2.761 \text{ \AA}$ ).

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

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

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

Figure 1: Polarisation contributions to the binding of  $\text{ArAu}^+$  as a function of internuclear separation  $R$ . The subscripts D,Q, and O indicate the inclusion of dipole, quadrupole and octopole polarisabilities respectively;  $B$  and  $\gamma$  are the dipole-quadrupole and second hyperpolarisabilities. 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  $\text{Au}^+$  ion.  $U_D(R)$  is the expression previously compared against to infer covalency within the complex.<sup>5</sup> ( $R_e = 2.730 \text{ \AA}$ ).

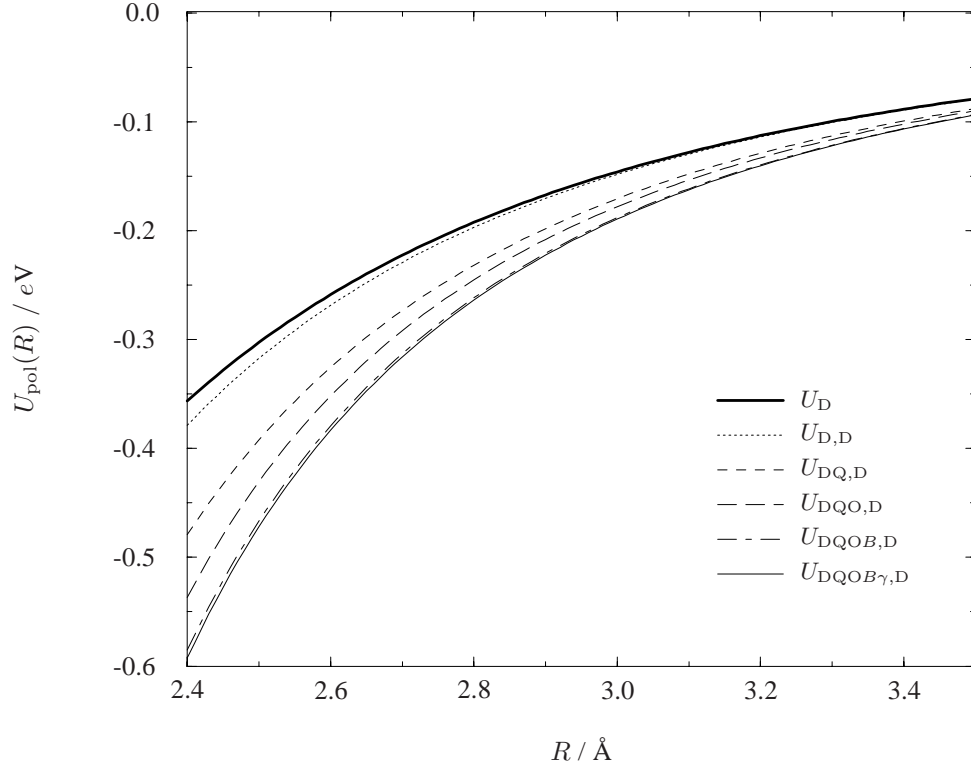


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The leftmost result is the expression previously compared against to infer covalency within the complex.<sup>5</sup>

( $R_e^{\text{ArAu}^+} = 2.730 \text{ \AA}$  and  $R_e^{\text{XeAu}^+} = 2.761 \text{ \AA}$ ).

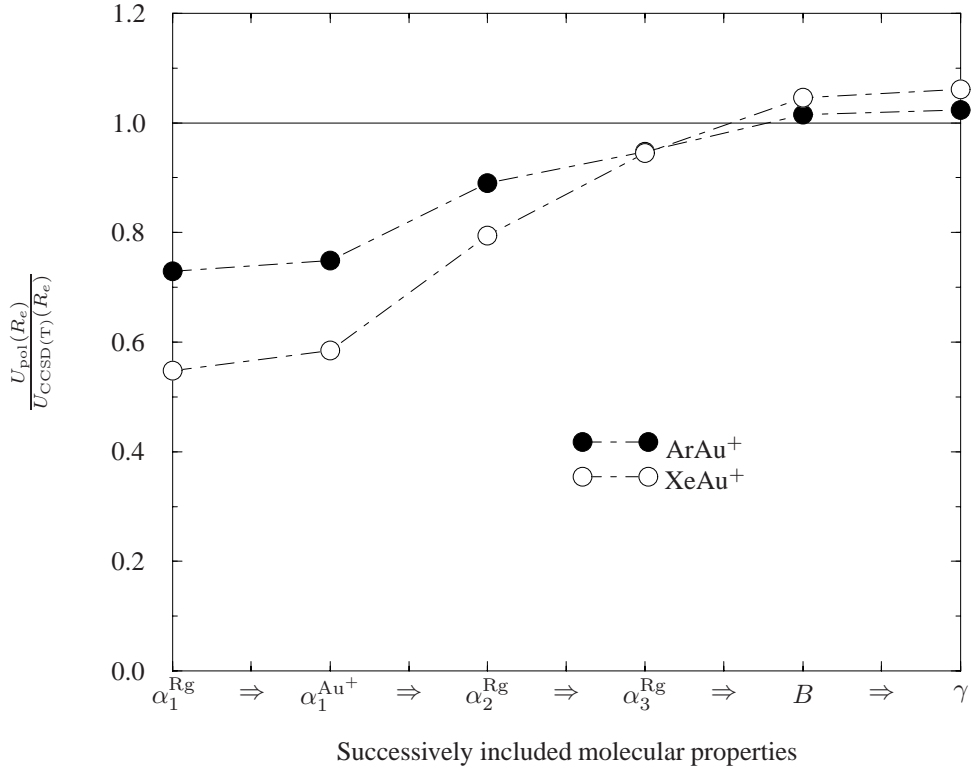


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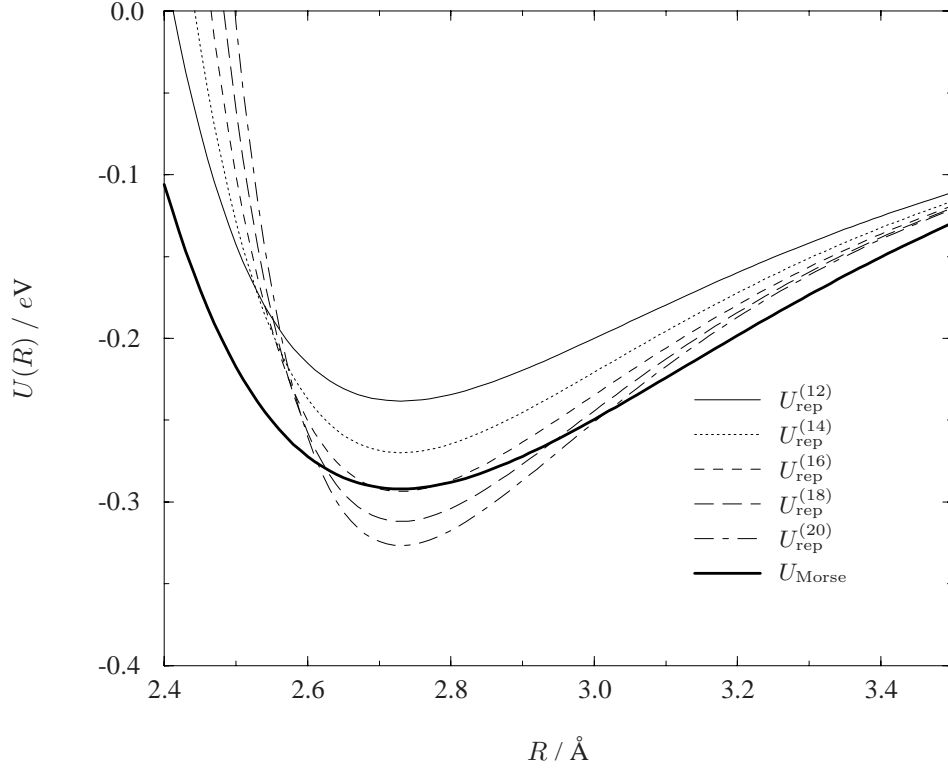


Figure 4: The potential energy surface for the interaction between Xe and  $\text{Au}^+$ , where  $R$  is the internuclear separation. The attractive contributions to binding are taken to be  $U_{\text{DQOB}\gamma, \text{D}}(R)$  and  $U_{\text{disp}}(R)$  of Eqs. (8) and (9), and an empirical repulsion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

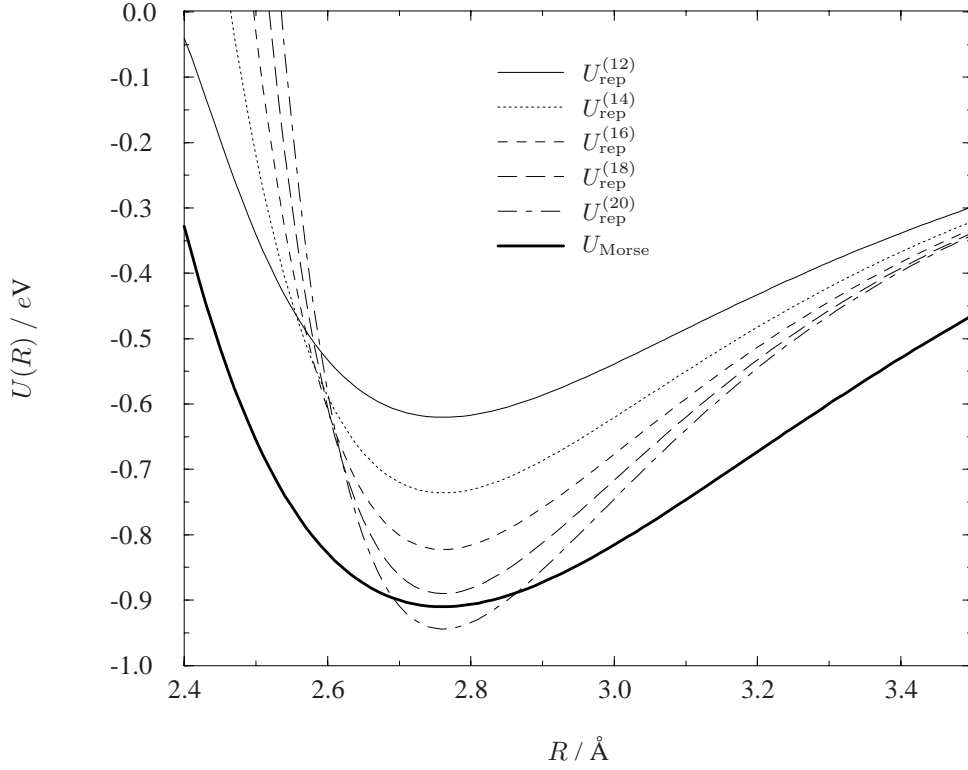


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