the current transport by trivalent charge carriers. This challenge can be managed, for example, with "Tubandt electrolysis" experiments.

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[18] The crystals were fixed by insertion into a corundum tube and filling of the remaining spaces with a hardening liquid cement.
[19] The applied dc voltage amounted to 6 V in both experiments. The sample was electrolyzed for 130 d in the case of the low-temperature electrolysis ($T = 250$ °C), and for 16 d in the case of the high-temperature electrolysis ($T = 650$ °C).
[20] With the use of nonreversible electrodes, the applied voltage must exceed the decomposition voltage of the compound in order to generate a constant flux of charge carriers. In the case of Nd^{3+}-β''-Al_2O_3, the decomposition voltage was determined in advance to be about 1.5–2 V.
[21] The degree of exchange refers to the original Na^+ content of the Na^+-β''-Al_2O_3 crystals used.
[22] The transference numbers for the electrolysis cannot be quantitatively determined because the absolute amount of transported charge carriers is not known. The EPMA data only represent the relative cation distribution on the surface. Transported cations which are located beneath the surface are not detected.

Extremely Strong s^2–s^2 Closed-Shell Interactions**

Ralf Wesendrup and Peter Schwerdtfeger*

Closed-shell interactions (CSI) range from extremely weak van der Waals forces, as for the helium dimer (dissociation energy, $E_d = 9.06 \times 10^{-2}$ kJ mol^{-1}),[1, 2] to strong aurophilic interactions (E_d up to 30 kJ mol^{-1})[3]. The strength of the latter lie almost in the order of covalent bonds, and strong CSI have recently been reviewed by Pyykkö.[4] The bonding situation in these compounds is described by an equal number of electrons in bonding and antibonding molecular orbitals. This gives rise to a bond order of zero and explains why CSI are generally so weak.

Unusually strong "closed-shell interactions" have recently been reported for the d^{10}-s^2 system Au^+–Hg (E_d = 179 kJ mol^{-1}, Table 1),[5] and for the related cationic gold rare gas (Rg) compounds $RgAu^+$ ($E_d = 126$ kJ mol^{-1}).[6] These

Table 1. Bond lengths r_e [Å] and dissociation energies E_d [kJ mol^{-1}] (not corrected for zero-point vibration) at various levels of theory.

	AuM		AuM		AuM^-	
	r_e	E_d	r_e	E_d	r_e	E_d
M = *Hg*$^+$[a]						
R-HF	2.700	119.4	–	–	3.293	13.4
R-MP2	2.528	197.2	2.630	56.3	2.838	58.1
R-CCSD	2.590	168.5	2.743	28.8	3.018	30.4
R-CCSD(T)	2.581	179.2	2.711	37.6	2.967	36.8
NR-HF	3.066	89.8	–	–	3.631	15.4
NR-MP2	2.794	145.9	2.883	41.7	3.016	59.3
M = *Ba*						
R-HF	2.979	125.7	3.131	138.8	3.322	105.4
R-MP2	2.711	319.0	2.848	292.0	2.998	163.3
R-CCSD	2.811	263.2	2.951	238.9	3.126	136.1
R-CCSD(T)	2.789	286.2	2.930	255.7	3.102	142.9
NR-HF	3.490	62.7	3.595	54.7	3.856	70.7
NR-MP2	3.055	169.1	3.146	138.4	3.325	127.4

[a] Results for $AuHg^+$ are taken from ref. [5].

cationic dimers fulfill the formal criterion for CSI since they consist of two interacting closed-shell fragments, the d^{10} gold cation and a closed-shell atom. However, significant charge transfer from the neutral atom to the gold cation at the equilibrium distance and low-lying alternative dissociation channels indicate a contribution from open-shell configurations to the bonding. Even though the degree of covalency in $RgAu^+$ and related species remains subject to discussion,[7] these compounds are clearly different from the aforementioned examples. Their highest occupied molecular orbitals

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(HOMO) are of bonding character and the resulting bond order is one, in line with the high dissociation energies. However, addition of two electrons to the low-lying antibonding σ* orbital would result in a bond order of zero and lead to the corresponding *anionic* gold compounds.[6]

Anionic diatomic closed-shell compounds have not been studied extensively,[8] and only few gold-containing examples were addressed so far.[5,6] In a study on alkaline-earth/alkali metal dimers Bauschlicher, Jr. et al reported the notable dissociation energy of 26 kJ mol^{-1} for the anion MgNa$^-$.[9] A simple MO picture cannot explain why this s^2-s^2 interaction gives rise to that particular stability and why MgNa$^-$ is even more stable than its neutral analogue MgNa. In the anion however, the negative charge at the Group 1 element gives rise to a dipole interaction (charge-induced dipole interaction,[10] CID). Such interactions are responsible for the stability of weakly bound species such as HeH$^-$, NeH$^-$, or ArH$^-$.[11] In addition, dispersion forces (D) are increased in the anionic molecule because the polarizability of the atomic anion is substantially higher than that of the neutral atom. These two forces can be expressed by Equation (1) using the London expression[12] for the dispersion force.

$$V^{A^-+B}(R) \cong V^{A^-B}_{CID}(R)+V^{A^-B}_{D}(R) = -\frac{1}{2}\frac{\alpha^B_D}{R^4}-\frac{3}{2}\frac{\alpha^{A^-}_D\alpha^B_D}{R^6}\frac{EA_A IE_B}{EA_A+IE_B} \quad (1)$$

A similar effect can be expected for anionic gold compounds. Owing to the strong relativistic contraction of its singly occupied 6s orbital gold possesses a very high electron affinity and diatomic gold compounds are characterized by unusually short bond lengths.[13] According to Equation (1) these factors should make the gold anion with a relatively small ionic radius the ideal candidate for strong CID and dispersion interactions. We therefore studied the series AuM$^+$, AuM, and AuM$^-$ for the s^2 atoms M = Hg and Ba by Hartree–Fock (HF), second-order Møller-Plesset (MP2), and coupled-cluster (CCSD(T)) methods.[14]

Successively filling up the antibonding $\sigma^*(6s_{Au}-6s_{Hg})$ orbital along the series AuHg$^+$, AuHg, and AuHg$^-$ has the expected influence on the geometry (Table 1). The calculated bond lengths increase from AuHg$^+$ to AuHg$^-$ in connection with a decreasing vibrational frequency at the correlated level. For the dissociation energy however, the trend is different. At the CCSD(T) level E_d drops drastically from 179 kJ mol^{-1} for AuHg$^+$ to 38 kJ mol^{-1} for AuHg, but it remains almost constant from AuHg to AuHg$^-$ at 37 kJ mol^{-1}. At the HF level neutral AuHg is even unbound and only the ionic species are stable. While it has been pointed out that removing an electron from a bonding orbital can increase the bond strength,[15] AuHg serves as an example for the reverse effect.[9] The bonding of AuHg$^-$ at coupled cluster level is

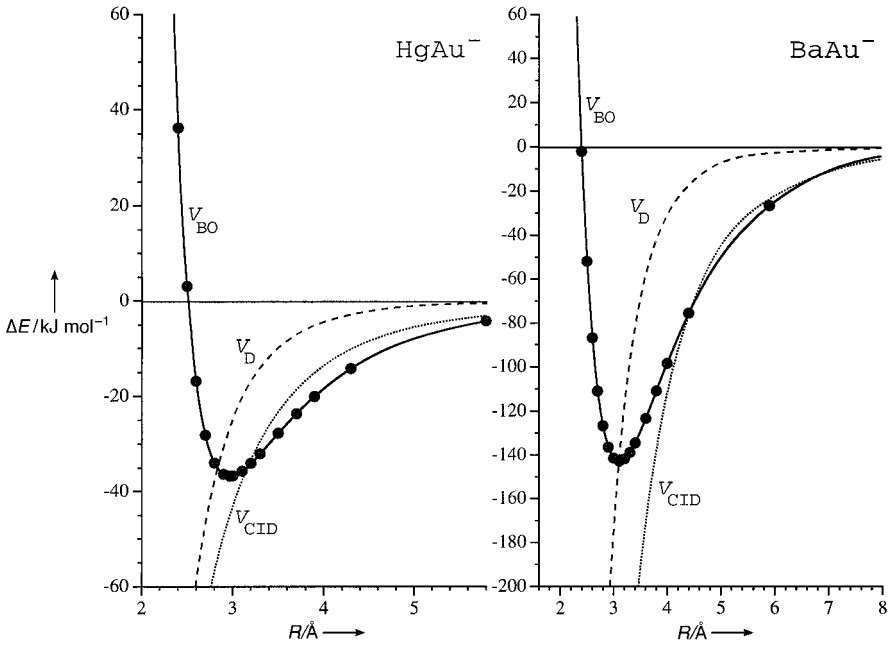

Figure 1. Born–Oppenheimer potential energy curves $V_{BO}(R)$ for AuHg$^-$ and AuBa$^-$. Also shown from the top to the bottom are the curves for the dispersion interaction $V_D(R)$ and the charge-induced dipole interaction $V_{CID}(R)$.

analyzed in Figure 1 in terms of CID and dispersion interactions. Calculated relativistic CCSD(T) polarizabilities were used for Au$^-$ and Hg and experimental values for the ionization energy of Au$^-$ and Hg, as listed in Table 2. It is evident from the greater slope of the $V_{CID}(R)$ curve that the interaction in AuHg$^-$ is predominantly of charged-induced nature. In contrast to anionic alkaline-earth/alkali metal dimers dispersion forces are of minor importance,[9] which explains why AuHg$^-$ is bound at the HF level in comparison with AuHg where dispersion prevails.[16]

Table 2. Calculated (CCSD(T)) ionization energies IE [eV] and static dipole polarizabilities α [au] for Au/Au$^-$, Ba, and Hg compared with experimental values or those from benchmark calculations.[34]

	CCSD(T)		Reference	
	IE	α	IE	α
Au	9.14	34.9	9.23	36.1[a]
Au$^-$	2.22	89.2	2.31	92.0[a]
Ba	5.16	278.6	5.21	268 ± 22
Hg	10.32	33.9	10.44	33.9

[a] Calculated value.

Ba is believed to have the highest polarizability of all neutral closed-shell atoms,[17] roughly three times that of Hg (Table 2). Neglecting higher order induction terms in the weak perturbation one would accordingly expect an approximately three times higher dissociation energy for AuBa$^-$ at bond lengths similar to those in AuHg$^-$. We note in passing that the much lower polarizability of Xe ($\alpha_D = 27.3$ au)[18] explains why calculations for the related AuXe$^-$ yield only a small interaction energy of 8 kJ mol^{-1} at a relatively long bond length of 4.18 Å.[6] In fact, the dissociation energy of AuBa$^-$ is almost four times higher than in AuHg$^-$ and amounts to 143 kJ mol^{-1} (Table 1) at the coupled-cluster level; a value

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that is usually associated with covalent bonds. The Mulliken population analysis of $AuBa^-$ based on the MP2 density reveals a slight participation from $Au(6p_\sigma)$ and $Ba(5d_\sigma)$ to the two σ-HOMOs thus reducing the Pauli-repulsion between the s^2 electron pairs. Besides this mere polarization effect the orbital population in the molecular fragments is practically unchanged from the population in separated Au^- and Ba. This rules out large contributions of excited higher states. Only a negligible charge transfer is observed in $AuBa^-$ (Mulliken charge $q_{Ba} = -0.04$) in line with the electron affinities of Au ($EA_{Au} = 2.31$ eV)[19] and Ba ($EA_{Ba} = 0.22$ eV).[20] These findings clearly demonstrate that $AuBa^-$ represents the strongest closed-shell interaction reported so far. As in $AuHg^-$ the interaction is mainly of CID character (Figure 1, using IP = 5.16 eV for Ba).[21] This is confirmed by the fact that even at the HF level $AuBa^-$ is bound by more than 100 kJ mol^{-1}. Moreover, a plot of $\lg(-\Delta E)$ over $\lg(R)$ for the potential energy curve $\Delta E(R)$ of $AuBa^-$ yields an almost perfect linear behavior and excellent agreement with the corresponding $V_{CID}(R)$ curve at distances of $R > 4$ Å.

The situation for the neutral and cationic molecules is distinctly different. Both $AuBa^+$ and AuBa exhibit a dissociation energy greater than 250 kJ mol^{-1} and clearly lie in the order of other covalently bound gold main group atom dimers.[22] In Table 3 we report vibrational–rotational constants for studied AuM compounds (M = Hg, Ba) for future spectroscopic measurements. The constants were derived from extended Morse potentials fitted to the CCSD(T) single points. Fit parameters for the Morse curves are also listed in Table 3.

Finally, one should consider if there are related charged diatomic compounds with similarly high dissociation energies. Preliminary MP2 calculations for a few selected $M_1M_2^+$ species (M_1 a Group 2 or 12 element and M_2 a Group 3 or 13 element) give $r_e = 2.201$ Å and $E_d = 174.0$ kJ mol^{-1} for BeB^+, $r_e = 3.283$ Å and $E_d = 24.9$ kJ mol^{-1} for BaB^+ (dissociating into Ba^+ and B), $r_e = 3.342$ Å and $E_d = 27.5$ kJ mol^{-1} for $HgTl^+$,[28] $r_e = 4.395$ Å and $E_d = 4.2$ kJ mol^{-1} for $BaTl^+$ (dissociating into Ba^+ and Tl). Similarly to $AuHg^+$ a high dissociation energy is only obtained if the ionization potentials of M_1 and M_2 become comparable in size thus resulting in large metal p-orbital participation and strong covalent bonding character. As a particular example we further mention the doubly charged $HeBe^{2+}$ with a very short bond length of $r_e \approx 1.40$ Å and a dissociation energy of $E_d \approx 86$ kJ mol^{-1}.[23]

For selected anionic (Group 1/11)–Ba diatomics preliminary MP2 calculations give the following bond lengths and dissociation energies: $r_e = 3.689$ Å and $E_d = 94.6$ kJ mol^{-1} for $CuBa^-$, $r_e = 3.757$ Å and $E_d = 83.9$ kJ mol^{-1} for $AgBa^-$, $r_e = 4.431$ Å and $E_d = 49.2$ kJ mol^{-1} for $LiBa^-$ and $r_e = 5.902$ Å and $E_d = 32.8$ kJ mol^{-1} for $CsBa^-$.[24] The corresponding values for $AuBa^-$ at the same computational level are $r_e = 3.458$ Å and $E_d = 112.9$ kJ mol^{-1}. It is evident that the bond lengths in the alkali metal containing dimers are too long to allow for efficient CID interactions which results from the diffuse and highly polarizable nature of the alkali metal anions. The less pronounced difference of $AuBa^-$ to its lighter homologues $CuBa^-$ and $AgBa^-$ can be attributed to relativistic effects. The relativistic contraction of the doubly occupied 6s orbital in Au^- reduces the ionic radius and allows a comparably short bond in $AuBa^-$. This relativistic bond contraction of $\Delta_R r_e = 0.173$ Å (at the MP2 level, see Table 1) greatly increases the CID interaction and overcompensates the relativistic reduction of the Ba polarizability ($\Delta_R \alpha_D = 37$ au).[25] It is this unique combination of a relativistically contracted short bond length and the large dipole polarizability of Ba which makes the extraordinarily strong s^2–s^2 interaction in $AuBa^-$ possible.

Computational Details

The nonrelativistic (NR) and scalar relativistic (R) energy-adjusted small-core pseudopotentials of the Stuttgart group were used to replace the inner 46 electrons for Ba and the inner 60 electrons for Au and Hg.[26] Large uncontracted (11s10p9d4f) correlation-consistent Gaussian type basis sets were used to describe the valence electrons. The basis sets were generated by numerically optimizing (9s9p6d4f) subsets of exponents at the second-order Møller-Plesset level (MP2) which were augmented by (2s1p3d) sets of diffuse functions.[27] Basis sets obtained by this procedure can successfully suppress of what is known as the basis set superposition error (BSSE).[28] The generated basis sets were first tested for the accurate description of atomic polarizabilities and ionization energies as these properties are crucial for binding in the anionic molecules. A finite field

Table 3. Spectroscopic constants as derived from the CCSD(T) potential energy curves; harmonic frequency ω_e [cm^{-1}], anharmonicity constant $\omega_e x_e$ [cm^{-1}], rotational constant B_e [10^{-1} cm^{-1}], centrifugal distortion constant D_e [10^{-8} cm^{-1}], vibration–rotational coupling constant α_e [10^{-4} cm^{-1}]. Parameters in atomic units for extended Morse fits to the CCSD(T) single points are also included. The extended Morse potential is defined as $V(R) = \sum_i A_i e^{-a_i(R-r_e)}$.

	$AuBa^+$	AuBa	$AuBa^-$	$AuHg^+$[a]	AuHg	$AuHg^-$
ω_e	149	123	94	139	103	64
$\omega_e x_e$	0.56	0.18	0.21	0.36	0.84	0.50
B_e	0.268	0.242	0.216	0.253	0.228	0.191
D_e	0.366	0.376	0.455	0.330	0.436	0.680
α_e	0.130	0.533	0.660	0.47	1.447	1.464
a_1	1.1810×10^{-1}	1.0450×10^{-1}	7.0600×10^{-2}	1.4330×10^{-1}	1.4895	2.0976
A_1	2.9900×10^{-1}	2.8580×10^{-1}	3.5040×10^{-1}	2.5460×10^{-1}	7.6900×10^{-2}	-5.9379×10^{-3}
a_2	1.6583	1.5691	2.6038×10^{-6}	2.2378	1.8186	1.1075
A_2	-2.5500×10^{-2}	-1.9300×10^{-2}	-8.3000×10^{-1}	-1.3600×10^{-2}	-6.3300×10^{-2}	1.2300×10^{-2}
a_3	-5.1600×10^{-2}	-6.6243×10^{-3}	-1.6300×10^{-2}	-2.6014	1.6910×10^{-1}	9.0250×10^{-1}
A_3	-1.6480×10^{-1}	-1.6930×10^{-1}	1.4502	2.8678×10^{-6}	7.3691×10^{-4}	-1.0100×10^{-2}
a_4	-2.0292	-1.8889	-3.2913×10^{-5}	2.0395	–	4.4480×10^{-1}
A_4	1.1655×10^{-6}	4.8447×10^{-7}	-6.3510×10^{-1}	-4.3644×10^{-4}	–	1.7600×10^{-2}

[a] Results for $AuHg^+$ are taken from ref. [5].

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model using external fields of 0.000, 0.001, 0.002 and 0.004 au was used to calculate the static dipole polarizabilities for Ba, Au/Au$^-$ and Hg. Table 2 shows the excellent agreement of our CCSD(T) properties with available reference data.

Calculations were performed at Hartree–Fock (HF), MP2, CCSD and CCSD(T) level using the programs Gaussian 98[29] and Aces II.[30] At least 20 single points were calculated to describe the potential curves and corrected for the BSSE using the counterpoise correction by Boys and Bernardi.[31] The corrected potential curves were fitted by an extended Morse potential (Table 3).[32] Spectroscopic parameters were derived from a numerical Numerov–Cooley procedure as implemented in MOLCAS 3.[33]

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A General Approach to L-(+)-Furanomycin and Some Stereoisomers and Analogues Using Furoisoxazoline Intermediates**

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In 1967 Katagiri et al. reported on the isolation of the antibiotic α-amino acid L-(+)-furanomycin (**1**) from the fermentation broth of *Streptomyces threomyceticus* (ATCC 15795).[2] L-(+)-Furanomycin shows considerable activity against different bacteria, for example *E. coli*.[2] Later, **1** was found to be charged to isoleucine tRNA by isoleucyl-tRNA synthetase from *E. coli* and incorporated into protein.[3]

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