Calculated Structures of SAu_3^+ and $S(AuPH_3)_3^+$

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Pseudopotential *ab initio* calculations on SAu_3^+ and $S(AuPH_3)_3^+$ closely reproduce the experimental Au–S–Au angles of monomeric $S(AuPR_3)_3^+$ (PR_3 = PPh_3, PPr^i_3) if both correlation and relativistic effects are included.

Attractions between formally closed-shell Au^I ($5d^{10}$) atoms occur in a number of structural motifs and lead to dimers, oligomers, chains and sheets.[1] At the *ab initio* level, correlation effects are necessary to obtain any attraction[2–5] and relativistic effects are partially responsible for its extraordinary strength.[2,3]

We have earlier considered the A-frame motif $E(AuPH_3)_2$, E = Se, Te,[3] and the (T_d or C_{4v} tetrapode) motif $E(AuPH_3)_4^+$, E = N, P, As,[4] with the same conclusions. Because the first monomeric $S(AuPR_3)_3^+$ systems, with R = Ph[6] and R = Pr^i,[7] have just been structurally characterized, we now consider the tripodal system $S(AuPH_3)_3^+$ as a model system for these experimentally known structures (Fig. 1).

Both Hartree–Fock (HF) and second-order Møller–Plesset (MP2) calculations were performed using GAUSSIAN 92 and either 11 or 19 valence-electron (11- or 19-VE) pseudopotentials.[8] In the 19-VE case, both relativistic and non-relativistic (R/NR) potentials were chosen. The Au–S distance was fixed at a typical experimental value of 232 pm. The other parameters were P–Au = 225, P–H = 141.7 pm and H–P–Au = 118.5°, S–Au–P = 180°. C_{3v} symmetry was assumed with two peripheral and one axial H for each PH_3 group. The phosphine-less core SAu_3^+ (C_{3v}) is included among the results in Table 1.

The key results are shown in Figs. 2 and 3 and in Table 1. In Fig. 2 the quasirelativistic (19-VE) curves give similar results for SAu_3^+ as found earlier in the A-frame motif[3] and the tetrapode.[4]

At the non-relativistic level without correlation (HF/NR) the energy minimum remains at Au–S–Au = 120°. The HF/R and MP2/NR levels give very flat minima. Only the MP2/R case gives a deep minimum (ΔE = 0.039 au) near the experimental Au–S–Au angles, β. These results underline the importance of both correlation as well as relativistic effects, in influencing the geometry of trigoldsulfonium cations.

This was without taking phosphine groups into account; it has been shown earlier, that their effect on the M–E–M (M = Cu, Au) angle is small.[3,4,9] The use of a PH_3 group to model the structures with higher PR_3 groups was found to be acceptable,[10] although this approach at the semiempirical level has been criticised.[11] The effect of the PH_3 groups is studied in Fig. 3 at the 11-VE/MP2/R level and is found to be quite small, both on ΔE and on the Au–S–Au angle. The angles obtained are near the experimental ones. Note that the phosphine with the larger cone angle (R = Pr^i) gives the larger experimental Au–S–Au angle, suggesting steric repulsion. In Table 1 we also give the force constant ($\partial^2E/\partial\beta^2$) for vibrational spectroscopy.

The Mulliken overlap populations are given in Table 2. The data for Au–Au are small or negative, also suggesting the lack

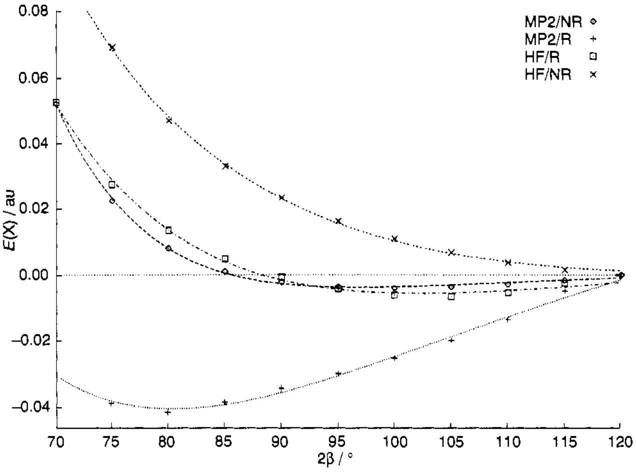

Fig. 2 Calculated bending energies of SAu_3^+ using 19 valence-electron pseudopotentials at four different levels of approximation

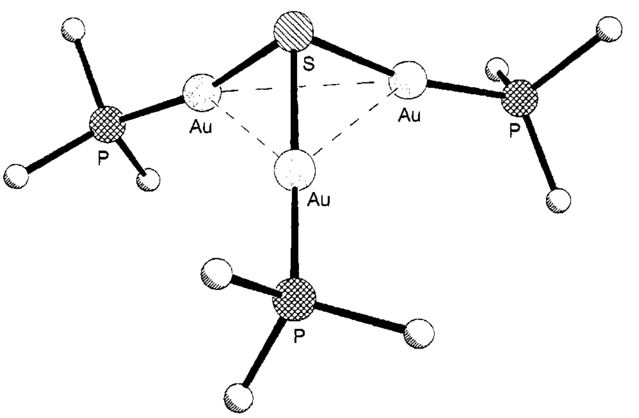

Fig. 1 Heavy atom skeleton of $S(AuPR_3)_3^+$ cations, modeled after the experimental data for $S(AuPPh_3)_3^+$ BF_4^- (ref. 6; only the *ipso*-C atoms of the phenyl groups are shown)

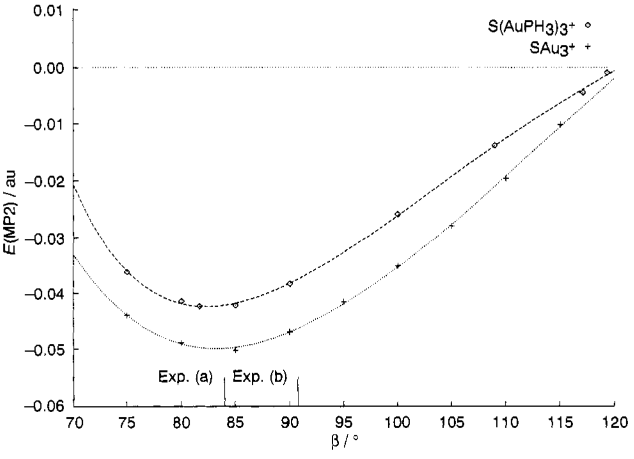

Fig. 3 Calculated bending energies of SAu_3^+ and $S(AuPH_3)_3^+$ at the 11-VE relativistic MP2 level. The experimental points (*a*) and (*b*) refer to refs. 6 and 7, respectively.

Table 1 The optimized Au–S–Au angle β_0, the corresponding Au–Au distance d, the energy decrease from D_{3h} geometry (β = 120°) ΔE and the force constant ($\partial^2E/\partial\beta^2$) of the calculated systems in comparison with the experimental data

System	Basis	Method	β_0/°	d/pm	ΔE/au	10^4 ($\partial^2E/\partial\beta^2$)/ au (°)^2
SAu_3^+	11-VE/R	HF	100.6	357	0.007	
	11-VE/R	MP2	83.3	308	0.048	1.469
	19-VE/R	HF	102.3	361	0.003	
	19-VE/R	MP2	80.5	302	0.039	1.378
	19-VE/NR	HF	120	402		
	19-VE/NR	MP2	96.8	344	0.003	
$S(AuPH_3)_3^+$	11-VE/R	HF	98.5	352	0.006	
	11-VE/R	MP2	82.3	305	0.043	1.865
$S(AuPPh_3)_3^+$	experimental data		84.0	312		
$S(AuPPr^i_3)_3^+$	experimental data		90.8	325		

Table 2 Au–Au, Au–S and Au–P Mulliken overlap populations (all systems were calculated at an Au–S–Au angle of 83.3°)

System	Basis	Method	Au–Au	Au–S	Au–P
SAu_3^+	11-VE/R	HF	−0.001	0.269	
	11-VE/R	MP2	−0.120	0.196	
	19-VE/R	HF	−0.285	0.276	
	19-VE/R	MP2	−0.488	0.209	
	19-VE/NR	HF	0.001	0.200	
	19-VE/NR	MP2	−0.363	0.187	
$S(AuPH_3)_3^+$	11-VE/R	HF	−0.005	0.288	0.486
	11-VE/R	MP2	−0.146	0.209	0.379

of any covalent driving mechanism between the gold atoms. The total atomic populations for $S(AuPH_3)_3^+$ (11-VE, MP2/R) are $S^{0.057}Au^{-0.207}P^{0.586}H_{ax}^{-0.015}\ H_{eq}^{-0.025}$. The Mulliken Au orbital populations are $6s^{0.88}5d^{9.63}6p^{0.63}5f^{0.07}$ in this nominally Au^I compound and the NBO set is $6s^{0.80}5d^{9.74}6p^{0.07}5f^{0.02}$.

The present Au–S–Au bond angles are only slightly smaller than those of H_3S^+, calculated to be 95.8° at the MP2 level.[12] In that case, however, the HF and MP2 geometries are closely similar, forbidding any comparison with the present case.

In conclusion, we have found a case where both correlation and relativistic effects are needed to reproduce the experimental Au–S–Au angle.

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