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Multiple bonds to gold: a theoretical investigation of XAuC (X = F, Cl, Br, I) molecules

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Abstract

Structures and spectroscopic properties are reported for the linear XAuC (X = F, Cl, Br, I) series of molecules and their related diatomic species at a high level of accuracy. The singles and doubles coupled cluster method including a perturbational correction for connected triple excitations, CCSD(T), with systematic sequences of new correlation consistent basis sets have been employed. Scalar relativistic effects have been accurately included by making use of relativistic effective core potentials. Extrapolation to the complete basis set limit has been used with accurate treatments of core–valence correlation and spin–orbit effects in order to accurately predict spectroscopic properties, as well as dissociation and atomization energies at 0 K of AuC, AuC⁺, AuF, AuCl, AuBr, AuI, and the XAuC molecules. The Au–C bond length in the FAuC molecule is predicted to be nearly identical to that calculated for AuC⁺, which makes it the shortest known for a neutral gold molecule. The Au–C and Au–F (0 K) bond dissociation energies in FAuC are predicted to be 92.5 and 93.1 kcal/mol, respectively, also making them some of the strongest known bonds to gold. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

In recent years, the chemistry of gold has received considerable attention in inorganic as well as theoretical chemistry (see, for example [1–4], and other references therein). Even though the chemistry of gold is dominated by single chemical bonds, it is well known that gold can form unusually strong chemical bonds due to relativistic effects [5]. Nevertheless, no genuine multiple bonds to gold are experimentally known, apart from certain types of carbenes, e.g., Au=CL₂⁺ and L₂C=Au=CL₂⁺ [6–8]. The strongest partial triple bond

was predicted in ab initio calculations to exist in AuC⁺ [2,3]. In 1998 this species was the subject of two theoretical studies, both carried out by Pyykkö and co-workers [2,3]; they evaluated the equilibrium bond length and dissociation energy using both all-electron quasirelativistic Douglas–Kroll (DK) and relativistic effective core potential (RECP) methods. These computations revealed a short Au–C bond distance of about 1.77 Å with an equilibrium dissociation energy to ground state atoms of 3.8 eV. In [3] an attempt to predict further triple bonds to gold, in particular for neutral species, was also reported and multiple-bond character was observed for Cl₂AuCH and Cl₂AuN. More recently, Pyykkö et al. [4] carried out additional calculations on AuC⁺ at the B3LYP and MP2 levels of theory as calibration calculations for the subsequent investigation on [Au=C=Au]²⁺ species.

The present work was stimulated by the lack of data on neutral molecules containing multiple bonds to gold,

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as well as the recent development of correlation consistent basis sets for Au. The series of XAuC molecules, where X is a halogen atom (F, Cl, Br, and I) were chosen since they were expected to perhaps have a multiple bond between Au and C by analogy with AuC⁺, assuming that the halogen atom would withdraw electron density from Au. In order to fully characterize these species, the molecular and spectroscopic properties have been evaluated at the coupled cluster level with the accurate inclusion of relativistic, core–valence, and spin–orbit effects. In order to determine the thermodynamic properties of these compounds, namely, dissociation and atomization energies, the related diatomic and atomic fragments have also been characterized at the same level of accuracy.

2. Methodology

The standard aug-cc-pVnZ basis sets [9,10] have been employed for the C, F, and Cl atoms. The newly developed aug-cc-pVnZ-PP sets [11] have been used for the Br and I atoms; these are a series of correlation consistent basis sets in conjunction with small-core relativistic pseudopotentials that leave 25 electrons to be handled explicitly for both bromine (3s²3p⁶3d¹⁰4s²4p⁵) and iodine (4s²4p⁶4d¹⁰5s²5p⁵). The Au basis sets corresponded to preliminary aug-cc-pVnZ-PP sets [12] that use a new small-core, energy consistent relativistic pseudopotential [13] that leaves 19 electrons (5s²5p⁶5d¹⁰6s¹) to be explicitly correlated in the ab initio calculations. The Hartree–Fock spd parts of the Au basis sets are analogous in size to those presented previously [11,14] for Tl–Rn, but the shells of correlating functions corresponded to 2d1f, 3d2f1g, 4d3f2g1h, and 5d4f3g2h1i for the cc-pVDZ-PP through cc-pV5Z-PP basis sets. Additional diffuse augmenting functions were also added in each angular symmetry to form the aug-cc-pVnZ-PP basis sets. These will be fully described in another publication, but are currently available upon request from the authors. In the remainder of the text, all of the basis sets mentioned above will be denoted as aVnZ.

Geometry optimizations and energy evaluations have been performed with the coupled cluster singles and doubles method with a perturbative correction for connected triple excitations [CCSD(T)] [15]. For all of the open-shell species [AuC (²Π), halogen atoms (²P), Au (²S), and C (³P)], the ROHF/UCCSD(T) method [16–18] [R/UCCSD(T)] has been employed. In the case of the triatomic species, geometry optimizations at the CCSD(T)/aVnZ (*n* = T, Q, 5) level have been carried out using numerical gradients as implemented in the MOLPRO program suite [19–21]. The CCSD(T)/aVTZ and CCSD(T)/aVQZ harmonic force fields have been evaluated in a Cartesian coordinate representation at the corresponding optimized geometry. As for the en-

ergy gradients, the hessian matrix was calculated numerically [20,21] by finite differences. For the diatomics, near-equilibrium potential energy functions (PEFs) were calculated by accurately fitting a total of 7 points to polynomial expansions in displacement coordinates. Spectroscopic parameters were then determined from the fitted PEFs by the usual second-order perturbation theory expressions [22]. In the R/UCCSD(T) calculations on the atomic fragments, fully symmetry equivalenced orbitals were used. If not otherwise mentioned, the frozen core approximation has been used throughout (core definitions: C,F 1s; Cl 1s2s2p; Br 3s3p3d; I 4s4p4d; Au 5s5p).

Complete basis set limits of the total energies have been obtained by using the mixed exponential/Gaussian extrapolation formula [23,24]

$$E(n) = E_{\text{CBS}} + B e^{-(n-1)} + C e^{-(n-1)^2}, \quad (1)$$

where *n* = 3, 4, ... refers to the cardinal number of the basis sets, *n* = 3 for the aVTZ basis, *n* = 4 for aVQZ, and so on. For the diatomic molecules, the extrapolated total energies were then fit as above to obtain CBS limit PEFs and spectroscopic constants. In the case of the triatomic species, increasing the cardinal number *n* of the basis sets systematically shortened the bond distances. This expected trend from using the hierarchical sequences of basis sets can be exploited to estimate the complete valence basis set limits for the equilibrium geometries. In the present study the 1/*X*³ extrapolation formula [25,26] was used to describe the convergence behavior of these geometries.

Corrections for taking into account core–valence correlation effects were then added to the CBS limit energies and geometries. This involved carrying out both energy evaluations and geometry optimizations (triatomics) using the weighted core–valence aug-cc-pwCVTZ basis sets [27] for the C, F, and Cl atoms, and analogous aug-cc-pwCVTZ-PP sets for the Br, I, and Au atoms [12]. The additional core–valence correlating functions in the latter basis sets were optimized for correlation of the (*n* – 1)spd shells for the halogens and the 5s5p electrons in the case of Au. This corresponded to the addition of 2s2p2d2f1g and 2s2p2d1f shells of functions for the halogens and Au, respectively, to the aug-cc-pVTZ-PP sets to form aug-cc-pwCVTZ-PP basis sets. In the remainder of the text, these basis sets will be denoted as awCVTZ. The core–valence (CV) corrections to the total energies have been calculated in each case as $\Delta E_{\text{CV}} = E_{\text{core+val}} - E_{\text{val}}$, where $E_{\text{core+val}}$ is the (R/U)CCSD(T) total energy obtained by correlating all electrons (except the 1s electrons of Cl) and E_{val} is the (R/U)CCSD(T) total energy obtained in the frozen core approximation, both in the same aug-cc-pwCVTZ basis set. For the diatomics, the ΔE_{CV} corrections have been added to the CBS energies at each bond distance

and then fitted to polynomial expansions as above. In regards to the geometrical parameters of the triatomic species, the core correlation corrections have been added to the extrapolated structures $r(\text{CBS, valence})$ as

$$r_e \simeq r(\text{CBS, valence}) + r(\text{awCVTZ, all}) - r(\text{awCVTZ, valence}), \quad (2)$$

where $r(\text{awCVTZ, all})$ and $r(\text{awCVTZ, valence})$ are the geometries optimized at the CCSD(T)/awCVTZ level correlating all and only valence electrons, respectively.

Last, in addition to accounting for the effects of scalar relativity by using small-core relativistic PPs (the small relativistic effects due to C, F, and Cl are ignored in this work), the impact of spin–orbit (SO) coupling has also been taken into account. Two approaches have been investigated in the present work and both use the spin–orbit parameters from the PPs in each case. For the open-shell AuC molecule the SO corrections ΔE_{SO} have been evaluated within the state-interacting approach using the MOLPRO program, i.e., spin–orbit eigenstates have been obtained by diagonalizing $H_{\text{el}} + H_{\text{SO}}$ in a basis of pure Λ –S electronic states. The spin–orbit matrix elements have been calculated at the internally contracted multireference configuration interaction (MRCI)/aVTZ level of theory [28]. The orbitals used in the MRCI calculations have been obtained using the state-averaged complete active space self-consistent field (CASSCF) method with a full valence active space. The same configurations were used as references in the MRCI work. In order to recover both first- and second-order spin–orbit effects, four doublet, as well as quartet, electronic states of each symmetry in the C_{2v} point group have been considered in the construction of $H_{\text{el}} + H_{\text{SO}}$ (16 doublets and 16 quartets). At each bond distance defining the PEF, the ΔE_{SO} corrections were added to the CBS energies corrected by core–valence effects and fitted to polynomial expansions in order to evaluate SO-corrected spectroscopic constants.

For all other molecules studied in this work, the spin–orbit configuration interaction (SO-CI) method [29] as implemented in the COLUMBUS program [30–33] was employed. In these cases the ΔE_{SO} corrections have been evaluated as the difference between a CI calculation without SO coupling and the SO-CI energy for the ground state. Because the spin–orbit interaction can couple configurations with different spin multiplicities, the SO-CI calculations included all possible singlet as well as triplet electronic states. As concerns the CI computations, the MRCI method has been employed throughout and the CASSCF orbitals used in COLUMBUS were obtained from the MOLPRO program. For the triatomic species, the spin–orbit corrections have been evaluated at the best estimate equilibrium structure, i.e., that obtained from Eq. (2). For the diatomics, the ΔE_{SO} corrections have been evaluated for each point

defining the PEF and added to the CBS energies corrected by core–valence effects and then fitted to polynomial expansions. This approach has also been followed for the open-shell AuC molecule (in this case doublet and quartet states have been considered) and essentially the same results as those obtained from the state-interaction method were obtained. For the lighter atomic species involved in this work, i.e., C, F, and Cl, where PPs were not employed, the experimental SO corrections (lowest spin–orbit level relative to the j -averaged energy) of Moore [34] have been used. Note that the small molecular SO effects arising from these elements are implicitly not included in the above calculations. The SO effects of all other atoms have been calculated using the SO-CI approach.

The equilibrium bond dissociation energies, D_e , have been determined as the difference between the minimum energy of the molecular species and the sum of the energy of the separated fragments at their equilibrium geometry. The zero-point energy (ZPE) corrections have been included by adding the appropriate zero-point energy differences (anharmonic for the diatomics and harmonic-only for the triatomics), and thus D_0 's have been derived from the D_e 's. Since only harmonic frequencies have been employed for the triatomics and they generally overestimate the “real” anharmonic ones, the zero-point corrections are expected to be slightly overestimated in these cases. Finally, the atomization energies at 0 K have been determined as the energy difference between the minimum energy of the triatomic species and the sum of the energy of the separated atomic fragments (in their ground electronic states).

All ab initio computations have been carried out using the MOLPRO suite of programs [19].

3. Results and discussion

In Table 1 the equilibrium geometries, spectroscopic parameters, and dissociation energies of AuC^+ ($X^1\Sigma^+$) and AuC ($X^2\Pi$) calculated at the coupled-cluster level of theory using the aVnZ ($n = T, Q, 5$) and awCVTZ basis sets are shown. The dependence with respect to basis set is observed to be regular for all properties and nearly converged even at the aVQZ level. From these results, it is also apparent that both the core–valence and spin–orbit corrections are very significant. In regard to the former, they decrease the Au–C distance by about 0.01 Å and increase the harmonic frequency by more than 20 cm^{-1} for both molecules. In addition, core–valence correlation increases the AuC⁺ and AuC dissociation energies by 7.5 and 4.4 kcal/mol, respectively. The spin–orbit corrections also strongly affect the molecular structure; the equilibrium bond length is decreased by 0.009 and 0.012 Å for AuC⁺ and AuC, respectively. Our best estimate for the equilibrium bond length of AuC⁺, 1.764 Å,

Table 1

Equilibrium geometries, spectroscopic parameters and dissociation energies of AuC^+ ($X^1\Sigma^+$) and AuC ($X^2\Pi$) computed at the (R/U)CCSD(T) level of theory^a employing different basis sets

	r_e (Å)	B_e (MHz)	α_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (kcal/mol)	Energy (hartree)
<i>AuC⁺</i>							
aVTZ	1.7920	13913.8	0.00358	808.11	5.02	69.17	−172.720161
aVQZ	1.7863	14002.3	0.00363	814.33	5.05	71.00	−172.754480
aV5Z	1.7852	14020.8	0.00361	815.91	5.03	71.53	−172.767128
CBS ^b	1.7845	14031.4	0.00361	816.81	5.03	71.83	−172.774489
awCVTZ (f.c.)	1.7893	13955.3	0.00361	808.35	4.96		−172.727160
awCVTZ (all)	1.7799	14103.0	0.00348	834.35	4.77		−173.074840
CBS + CV ^c	1.7753	14176.4	0.00348	842.59	4.84	79.3	−173.122215
CBS + CV + SO ^d	1.7640	14359.0		830.91		81.0 ^e	−173.128511
<i>AuC</i>							
aVTZ	1.8637	12863.3	0.00378	691.23	4.72	62.75	−173.042183
aVQZ	1.8570	12957.4	0.00383	697.58	4.77	64.25	−173.077579
aV5Z	1.8553	12980.5	0.00382	699.71	4.71	64.77	−173.090601
CBS ^b	1.8544	12993.7	0.00381	700.94	4.68	65.1	−173.098181
awCVTZ (f.c.)	1.8610	12899.7	0.00380	691.54	4.66		−173.049087
awCVTZ (all)	1.8515	13034.6	0.00367	713.00	4.66		−173.396546
CBS + CV ^c	1.8450	13125.7	0.00368	722.17	4.66	69.5	−173.445687
CBS + CV + SO ^d	1.8330	13297.7		729.09		69.9 ^f	−173.450057

Extrapolated results to the valence CBS limit, core–valence, and spin–orbit corrected values are also reported.

^a (f.c.) and (all) Denote calculations correlating only valence and all electrons, respectively.

^b Geometrical and spectroscopic parameters evaluated from the CBS PEF: see text.

^c Geometrical and spectroscopic parameters evaluated from the CBS + ΔE_{CV} PEF: see text.

^d Geometrical and spectroscopic parameters evaluated from the CBS + ΔE_{CV} + ΔE_{SO} PEF: see text.

^e A ZPE correction of −1.16 kcal/mol yields a best estimate D_0 of 79.8 kcal/mol for dissociation to Au^+ and C^3P .

^f A ZPE correction of −0.99 kcal/mol yields a best estimate D_0 of 68.9 kcal/mol for dissociation to Au and C^3P .

is in good qualitative agreement with the previous work of Pyykkö and co-workers [2–4], who used valence-only electron correlation and smaller basis sets than those utilized in the present work. In regards to the dissociation energy of AuC^+ , our best equilibrium (CBS + CV + SO) and zero-point corrected values are 81.0 and 79.8 kcal/mol, respectively. The latter is in good agreement with the current experimental estimate, 77.4(10) kcal/mol [7], which was obtained from the photodissociation appearance threshold of AuCH_2^+ . Previous theoretical determinations of D_e were also carried out by Pyykkö and co-workers [2,4] at various levels of theory. Their valence-only DK-CCSD(T) result [2] of 81.3 kcal/mol was calculated with a basis set including 2d-type polarization functions on C and up to 4f-type functions on Au and is remarkably similar to our best estimate. This same study demonstrated that scalar relativistic effects are responsible for increasing the bond dissociation energy of AuC^+ by over 80 kcal/mol at the CASPT2 level of theory, as well as decreasing the equilibrium bond length by 0.5 Å.

Of all the molecules studied in this work, only in the case of AuC^+ did the CCSD T_1 diagnostic [35,36] reach a level (0.050 at r_e) that might indicate potential inaccuracies due to nondynamical correlation effects. In order to benchmark the performance of CCSD(T) in this case, large-scale internally contracted MRCI calculations [37,38] were carried out with the cc-pwCVTZ basis set,

but only correlating the valence electrons. Two different CAS active spaces were used in these calculations, a full valence active space denoted (5221) and the full valence space with the addition of the Au 6p orbitals, denoted (6331). In the latter case the MRCI reference function was restricted to have a maximum of only 2 electrons in these 6p-like orbitals. The comparison of CCSD(T) with these MRCI calculations are shown in Table 2. With the standard (5221) reference function, both MRCI and MRCI + Q (MRCI with the addition of the multireference Davidson correction for higher excitations [39–41]) yield an equilibrium bond length longer than CCSD(T) by as much as 0.015 Å. In this case the +Q correction actually slightly shortens the bond length relative to MRCI. Also shown in Table 2 are CASPT2 results [42,43] with this active space, which fairly closely mimics the MRCI and MRCI + Q values in this case. It should be noted that the present CASPT2 calculations with the (5221) active space differ from the previous all-electron calculations by Barysz and Pyykkö [2], who did not include the 5d orbitals in their active space. Their smaller active space evidently results in much shorter bond distances (shorter than CCSD(T) by 0.055 Å). The agreement between CCSD(T) and MRCI is much improved when the larger (6331) reference function is used in the MRCI. In this case the MRCI bond length is only about 0.002 Å longer than CCSD(T) with a harmonic frequency smaller by about 13 cm^{-1} . Clearly

Table 2
Comparison of CCSD(T) spectroscopic constants calculated for AuC⁺ with results using multireference methods^a

	r_e (Å)	α_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	Energy (hartree)
CCSD(T)	1.7862	0.00364	813.1	4.9	-172.716753
MRCI(5221)	1.8014	0.00416	809.6	4.9	-172.669584
MRCI + Q(5221)	1.8007	0.00430	828.9	5.1	-172.706149
CASPT2(5221)	1.7983	0.00469	830.2	5.2	-172.727284
MRCI(6331)	1.7879	0.00371	800.1	5.0	-172.683134
MRCI + Q(6331)	1.7902	0.00363	800.2	4.6	-172.712158
CASPT2(6331)	1.8056	0.00444	739.7	7.3	-172.724590

^a The cc-pwCVTZ basis set is used throughout. The notation (5221) refers to a full valence active space, while (6331) includes the Au 6p orbital. See the text.

in this case the larger active space that includes the Au 6p orbitals is essential in order to recover sufficient dynamical correlation to compare well with CCSD(T). Unfortunately, these MRCI calculations are computationally very expensive as they involve about 15,000 reference configurations, which result in nearly 25 million variational parameters (corresponding to 1.3 billion uncontracted configurations). Curiously, the CASPT2 method in this larger active space yields spectroscopic constants in worse agreement with CCSD(T). In any event, the large reference function MRCI calculations do tend to favor the CCSD(T) results, and hence the latter are expected to be very reliable in this case.

The calculated CCSD(T) equilibrium geometries, spectroscopic parameters, and dissociation energies of the diatomic gold halides (AuX, X = F, Cl, Br, I) are summarized in Table 3 where they are also compared to the available experimental values. There have also been numerous other theoretical studies of these molecules and the reader is directed to [44] and references therein for AuF, AuCl, and AuBr, as well as [45] and references therein for AuI. This is the first study that has used both highly correlated wavefunctions and systematic sequences of basis sets that approach the CBS limit. As is readily apparent from Table 3, the spectroscopic constants are rapidly convergent towards the apparent CBS limit. The differences between the aVTZ and CBS limit dissociation energies range from just +1.8 to +3.7 kcal/mol, while the analogous values for the equilibrium distances are -0.007 to -0.017 Å. As for AuC⁺ and AuC, the spin-orbit and particularly the core-valence corrections are significant. The latter corrections decrease the bond lengths by more than 0.01 Å and the extent of this correction increases along the series from AuF to AuI. The effect of core-valence correlation on the dissociation energies is more modest, ranging from just 0.8 to 1.6 kcal/mol. As concerns the spin-orbit corrections, their extent is smaller than for AuC⁺ or AuC; in fact, they decrease the distances by only about 0.004–0.005 Å. The SO effects on D_e are only appreciable for AuBr and AuI, -2.6 and -5.6 kcal/mol, respectively, due mainly to the large atomic SO splittings.

Upon comparison of the spectroscopic constants to experiment, excellent agreement is observed after all of the contributions are accounted for. In fact our best estimate equilibrium bond lengths for AuF, AuCl, and AuBr differ from the accurate experimental values by less than 0.001 Å in each case. The deviation from experiment for AuI is a bit larger, -0.0046 Å, but at least half of this can be attributed to small errors due to the PP on iodine as discussed in [11]. In general the harmonic frequencies are also in excellent agreement, being generally somewhat too large by a few cm⁻¹. Accurate comparison of the ab initio dissociation energies to experiment is more difficult since the experimental values are estimates based either on pure rotational spectra [46–49] or a kinetic study using mass spectrometry [45]. Certainly, the overall trend of D_e decreasing as the halogen ranges from F to I is well reproduced by our CCSD(T) calculations. Based on our experience with similar mercury species [50], we expect the present CBS + CV + SO values to be accurate to within 1–2 kcal/mol.

The equilibrium geometries, harmonic frequencies, and total energies of the linear XAuC (X = F, Cl, Br, I) series of molecules ($X^1\Sigma^+$) calculated at the coupled-cluster level of theory are reported in Table 4. First of all, from these results it is observed that, as expected, the Au–C distance increases by enlarging the halogen atom involved, i.e., the Au–C bond lengthens along the series from FAuC to IAuC. As concerns the basis set convergence, we notice that there is a very small shortening of the distances from the CCSD(T)/aV5Z level to the CBS limit, i.e., of about 0.001–0.002 Å, with the exception of the Cl–Au bond which shortens by about 0.004 Å. Presumably this latter convergence would be improved upon using the aug-cc-pV($n+d$)Z basis sets for Cl [51]. It should also be noted that the contributions from core-valence correlation enlarge along the series for the X–Au bond but only slightly for the Au–C distance. In the latter case they increase from just 0.004 Å in FAuC to 0.006 Å in IAuC. In regards to the X–Au bond, the core-valence corrections vary from 0.003 Å (FAuC) to 0.012 Å (IAuC). The lengthening of all the bond lengths is also reflected by the lowering of the stretching frequencies in moving

Table 3

Equilibrium geometries, spectroscopic parameters, and dissociation energies of the AuX (X = F, Cl, Br, I)^a molecules ($X^1\Sigma^+$) computed at the CCSD(T) level of theory employing different basis sets

	r_e (Å)	B_e (MHz)	α_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (kcal/mol)	Energy (hartree)
<i>AuF</i>							
aVTZ	1.9422	7732.1	0.00184	540.98	2.79	66.75	-234.894392
aVQZ	1.9379	7766.2	0.00183	545.68	2.79	68.00	-234.949422
aV5Z	1.9361	7781.3	0.00183	546.80	2.78	68.40	-234.969511
CBS	1.9350	7790.1	0.00183	547.45	2.77	68.6	-234.981202
awCVTZ (f.c.)	1.9408	7743.4	0.00183	542.26	2.79		-234.906143
awCVTZ (all)	1.9292	7836.6	0.00185	554.11	2.83		-235.256278
CBS + CV	1.9235	7883.2	0.00185	559.36	2.81	69.4	-235.331385
CBS + CV + SO	1.9182	7927.0		560.34		70.2 ^b	-235.336930
Expt. ^f	1.9184	7925.0	0.00187	563.70	3.27	69	
<i>AuCl</i>							
aVTZ	2.2303	3421.3	0.00054	368.64	1.29	64.64	-594.939319
aVQZ	2.2216	3448.1	0.00054	371.55	1.29	66.78	-594.989147
aV5Z	2.2161	3465.3	0.00054	373.82	1.30	67.77	-595.007433
CBS	2.2129	3475.4	0.00054	375.16	1.31	68.35	-595.018082
awCVTZ (f.c.)	2.2234	3442.4	0.00054	369.79	1.31		-594.949823
awCVTZ (all)	2.2128	3475.6	0.00054	378.24	1.34		-595.518502
CBS + CV	2.2024	3508.3	0.00054	383.66	1.35	69.2	-595.586823
CBS + CV + SO	2.1987	3520.4		389.05		69.3 ^c	-595.591885
Expt. ^g	2.1990	3519.2	0.00054	383.30	1.46	72/66 ± 3 ^h	
<i>AuBr</i>							
aVTZ	2.3459	1629.8	0.00018	256.14	0.69	60.23	-550.909084
aVQZ	2.3391	1639.3	0.00018	258.51	0.67	62.31	-550.955874
aV5Z	2.3360	1643.7	0.00018	259.28	0.65	63.03	-550.972726
CBS	2.3342	1646.3	0.00018	259.73	0.64	63.5	-550.982532
awCVTZ (f.c.)	2.3419	1635.5	0.00018	256.45	0.67		-550.918323
awCVTZ (all)	2.3290	1653.7	0.00019	262.64	0.69		-551.961926
CBS + CV	2.3215	1664.3	0.00018	265.87	0.67	64.5	-552.026185
CBS + CV + SO	2.3181	1669.2		271.68		61.8 ^d	-552.031227
Expt. ^g	2.3184	1668.8	0.00018	264.38	0.73	68/50 ± 5 ^h	
<i>AuI</i>							
aVTZ	2.5002	1047.5	0.00010	209.19	0.47	57.21	-432.049387
aVQZ	2.4922	1054.3	0.00010	210.83	0.45	59.33	-432.096661
aV5Z	2.4887	1057.2	0.00010	211.16	0.45	60.03	-432.113073
CBS	2.4867	1059.0	0.00010	211.36	0.46	60.4	-432.122616
awCVTZ (f.c.)	2.4919	1054.5	0.00010	209.43	0.46		-432.060548
awCVTZ (all)	2.4755	1068.5	0.00010	214.76	0.47		-433.105404
CBS + CV	2.4705	1072.9	0.00010	216.72	0.46	62.0	-433.167512
CBS + CV + SO	2.4665	1076.4		217.31		55.2 ^e	-433.173790
Expt. ⁱ	2.4711	1072.4	0.00010	215.77	0.50	66/52–64 ^h	

Extrapolated results to valence correlation limit, core–valence and spin–orbit corrected values are also reported and compared to available experimental data.

^a Spectroscopic parameters evaluated for the main isotopic species: AuF, Au³⁵Cl, Au⁷⁹Br and Au¹²⁷I. Also see the footnotes to Table 1.

^b A ZPE correction of -0.78 kcal/mol yields a best estimate D_0 of 69.4 kcal/mol.

^c A ZPE correction of -0.53 kcal/mol yields a best estimate D_0 of 68.7 kcal/mol.

^d A ZPE correction of -0.37 kcal/mol yields a best estimate D_0 of 61.4 kcal/mol.

^e A ZPE correction of -0.30 kcal/mol yields a best estimate D_0 of 55.0 kcal/mol.

^f Ref. [47].

^g Ref. [48].

^h Ref. [45].

ⁱ Ref. [49].

from FAuC to IAuC. In addition, by comparing the results reported in Tables 3 and 4, one can notice that while for X=F the halogen–gold distance decreases between the diatomic and triatomic species (by about 0.02 Å), it increases by about 0.03, 0.04, and 0.06 Å for X = Cl, Br, and I, respectively. This implies that

for X=F the X–Au bond is weaker in the diatomic than in the triatomic species, while the opposite is true for the other halogen atoms.

On the basis of the results collected in Tables 1 and 3, strong spin–orbit effects on the bond distances are also expected for the triatomic species. Thus, it should be ex-

Table 4

Equilibrium geometries, harmonic frequencies and energies of the linear XAuC (X = F, Cl, Br, I)^a molecules (X¹Σ⁺) computed at the CCSD(T) level of theory^b employing different basis sets

	$r_e(\text{X-Au})$ (Å)	$r_e(\text{Au-C})$ (Å)	ω_1 (cm ⁻¹)	ω_2 (cm ⁻¹)	ω_3 (cm ⁻¹)	Energy (hartree)
<i>FAuC</i>						
aVTZ	1.9161	1.7850	174.1	617.2	911.5	-272.812365
aVQZ	1.9121	1.7798	177.6	622.5	921.2	-272.875552
aV5Z	1.9106	1.7789				-272.898003
CBS ^c	1.9090	1.7780				-272.911061
awCVTZ (f.c.)	1.9149	1.7831				-272.826595
awCVTZ (all)	1.9119	1.7792				-273.231355
CBS + CV ^d	1.9060	1.7741				-273.315820
ΔE_{SO} (kcal/mol)						-4.83
<i>ClAuC</i>						
aVTZ	2.2528	1.8127	140.0	381.9	860.9	-632.831384
aVQZ	2.2474	1.8078	130.5	384.6	864.0	-632.888832
aV5Z	2.2436	1.8072				-632.909301
CBS ^c	2.2396	1.8066				-632.921206
awCVTZ (f.c.)	2.2478	1.8108				-632.843355
awCVTZ (all)	2.2442	1.8064				-633.466764
CBS + CV ^d	2.2360	1.8022				-633.544615
ΔE_{SO} (kcal/mol)						-4.88
<i>BrAuC</i>						
aVTZ	2.3762	1.8198	119.6	258.5	842.0	-588.793408
aVQZ	2.3726	1.8148	131.9	261.4	849.2	-588.847794
aV5Z	2.3703	1.8140				-588.866961
CBS ^c	2.3679	1.8132				-588.878106
awCVTZ (f.c.)	2.3731	1.8181				-588.804927
awCVTZ (all)	2.3658	1.8126				-589.902757
CBS + CV ^d	2.3606	1.8077				-589.975936
ΔE_{SO} (kcal/mol)						-4.91
<i>IAuC</i>						
aVTZ	2.5512	1.8314	113.5	203.8	817.8	-469.922257
aVQZ	2.5476	1.8263	80.7	203.4	822.6	-469.976796
aV5Z	2.5455	1.8254				-469.995502
CBS ^c	2.5433	1.8245				-470.006374
awCVTZ (f.c.)	2.5456	1.8300				-469.935337
awCVTZ (all)	2.5333	1.8238				-471.034264
CBS + CV ^d	2.5310	1.8183				-471.105301
ΔE_{SO} (kcal/mol)						-4.80

Extrapolated results to valence correlation limit, core–valence corrected values and spin–orbit corrections are also reported.

^a Harmonic frequencies evaluated for the main isotopic species: FAu¹²C, ³⁵ClAu¹²C, ⁷⁹BrAu¹²C and ¹²⁷IAu¹²C. ω_1 = XAuC bend, ω_2 = Au–X stretch, ω_3 = Au–C stretch.

^b (f.c.) and (all) Denote calculations correlating only valence and all electrons, respectively.

^c CBS geometries evaluated from the CCSD(T)/aVnZ geometries using the X⁻³ extrapolation technique: see text. CBS energies evaluated from the CCSD(T)/aVnZ energies using the mixed exponential/Gaussian function: see text.

^d Best estimated equilibrium geometries would be obtained by adding approximate SO effects of -0.01 Å to r_{AuC} and -0.005 Å to r_{XAu} . See the text.

pected that the inclusion of SO coupling will further shorten the both distances in each XAuC molecule by about 0.01 Å for r_{AuC} and by about 0.005 Å for r_{XAu} . These shifts should be applied to the CBS + CV values of Table 4 to yield our best estimates for the equilibrium geometries of these molecules.

The equilibrium and zero-point corrected dissociation energies for the X–Au and Au–C bonds and 0 K atomization energies of the XAuC (X=F, Cl, Br, I) triatomic species are reported in Table 5. As expected, all dissociation energies increase by enlarging the basis set and positive core–valence contributions have been ob-

tained in each case. For each of the dissociation paths considered, the dissociation energy decreases along the series of molecules; this confirms the weakening of the bonds in going from FAuC to IAuC.

From Table 5 it can also be observed that for all the species investigated, the dissociation of the X–Au and Au–C bonds are practically isoenergetic; i.e., nearly the same amount of energy is required to break each of these bonds. More precisely, the two D_e 's coincide within 1 kcal/mol for both FAuC and ClAuC, while $D_e(\text{Au–C})$ is slightly larger than $D_e(\text{Au–X})$ for BrAuC and IAuC. It should also be noted that for all molecules

Table 5

Equilibrium and zero-point corrected dissociation and atomization energies of XAuC (X = F, Cl, Br, I) evaluated at the coupled-cluster level

	XAuC \rightarrow X ⁻ + AuC ⁺	XAuC \rightarrow X(² P) + AuC	XAuC \rightarrow AuX + C(³ P)	$\sum D_0$
<i>FAuC</i>				
aVTZ	215.03	89.36	85.36	
aVQZ	215.86	91.07	87.32	
aV5Z	216.06	91.50	87.87	
CBS	216.17	91.74	88.18	156.81
CBS + CV ^a	217.3	93.1	93.2	162.6
ΔE_{SO} ^b	0.88	1.70	1.25	2.09
ZPE ^c	-1.55	-1.72	-1.93	-2.71
Best estimate D_0 ^d	216.6	93.1	92.5	162.0
<i>ClAuC</i>				
aVTZ	192.13	71.00	69.11	
aVQZ	192.71	73.25	70.73	
aV5Z	193.21	74.16	71.16	
CBS	193.50	74.69	71.40	139.76
CBS + CV ^a	194.9	76.1	76.5	145.7
ΔE_{SO} ^b	0.93	1.30	1.60	1.69
ZPE ^c	-1.00	-1.17	-1.63	-2.16
Best estimate D_0 ^d	194.8	76.3	76.5	145.1
<i>BrAuC</i>				
aVTZ	186.85	61.74	64.25	
aVQZ	187.23	63.91	65.85	
aV5Z	187.48	64.64	66.37	
CBS	187.63	65.06	66.67	130.12
CBS + CV ^a	188.8	66.4	71.4	135.9
ΔE_{SO} ^b	0.54	-1.45	1.65	-1.06
ZPE ^c	-0.80	-0.97	-1.59	-1.96
Best estimate D_0 ^d	188.5	64.0	71.5	132.9
<i>IAuC</i>				
aVTZ	180.63	51.53	57.06	
aVQZ	180.70	53.53	58.46	
aV5Z	180.80	54.22	58.96	
CBS	180.90	54.62	59.25	119.69
CBS + CV ^a	182.4	56.4	63.9	125.9
ΔE_{SO} ^b	-0.87	-6.39	0.76	-6.00
ZPE ^c	-0.54	-0.71	-1.40	-1.70
Best estimate D_0 ^d	181.0	49.3	63.3	118.2

Values in kcal/mol.

^a Core-valence (CV) corrections evaluated from frozen core and all electrons computations at the (R/U)CCSD(T)/awCVTZ level: see text.^b Spin-orbit (SO) corrections evaluated at the MRCI/aVTZ level: see text.^c Zero-point corrections (ZPE) evaluated from the CCSD(T)/aVQZ (an)harmonic frequencies: harmonic frequencies for triatomics and anharmonic frequencies for diatomic species.^d ZPE and SO corrections added to the CBS + CV values.

the core-valence corrections are very significant and larger for $D_e(\text{Au}-\text{C})$ than for $D_e(\text{X}-\text{Au})$, which is the same trend as observed in the analogous diatomic species. The zero-point corrections, obtained at the CCSD(T)/aVQZ level, are fairly small, of the order of 1–2 kcal/mol. From this table, it is also apparent that the SO effects are small but not negligible in most of the cases. Specifically, the SO contributions are generally positive and of the order of 1–2 kcal/mol. In the case of IAuC, however, a large negative (about -6 kcal/mol) correction has been calculated for the dissociation of the Au-X bond. This arises from the large atomic zero-field splitting in the iodine atom dominating the smaller second-order SO effect in the closed-shell IAuC molecule. By comparing the dissociation energies reported in Tables 3 and 5,

the same conclusions drawn by comparing the equilibrium bond lengths reported in Tables 3 and 4 are obtained: the F-Au bond is stronger in FAuC than in the diatomic AuF species, while the opposite is true for the other halogens. Also shown in Table 5 are the dissociation energies leading to ionic products, which are clearly much more energetic. For these D_e s the core-valence and spin-orbit corrections are relatively small; both are less than 2 kcal/mol in all cases.

In Table 5 the 0 K atomization energies for each of the XAuC molecules are also collected. As expected from the individual bond dissociation energies, core-valence corrections are very significant, on the order of 5–6 kcal/mol. In regards to spin-orbit corrections, they are positive for FAuC and ClAuC (~2 kcal/mol) and nega-

tive for the other molecules. Last, the zero-point corrections are small but not negligible, being on the order of 2–3 kcal/mol.

Lastly, it is also interesting to report the results from a natural bond orbital (NBO) analysis [52,53] on the XAuC species. These calculations were carried out at the CBS + CV geometries at the RHF/aVDZ level of theory using the NBO 5.0 program [54] as implemented in Gaussian98 [55]. The natural population analysis (NPA) charges on carbon are calculated to be positive and essentially unchanged along the XAuC series (from +0.15 in FAuC to +0.12 in IAuC), while the natural charges on Au are also positive and slightly decrease from FAuC to IAuC (from +0.66 to +0.46). On the other hand, the halogen atoms are strongly negative with their charges decreasing in magnitude from 0.80 in FAuC to 0.58 in IAuC. In addition, the NBO analysis does indicate a weak triple bond between carbon and gold for all four species. In each case the π bonds arise from electron donation from the gold d_{π} orbitals to the carbon p_x and p_y orbitals. On the other hand, the halogen–gold interactions are determined to be ionic in character, i.e., no bonding orbitals are found between these two atoms in all cases. Since AuC^+ has also been proposed to involve a partial triple bond [3], the NBO analysis was also carried out for this species. In this case, the NPA charges on Au and C were nearly the same, +0.59 on gold and +0.41 on carbon, and one σ and two π bonds were also indicated from the NBO analysis as in XAuC. In general, the NBO results appear to correlate well with the trends observed among the calculated bond lengths and dissociation energies. In the case of FAuC, its AuC distance is actually slightly shorter than that of AuC^+ , which correlates with a slightly larger natural atomic charge on gold in the former. As the charge on gold decreases from FAuC to IAuC, the AuC distance increases and its bond energy decreases. A similar destabilization effect has been previously discussed by Pyykkö and Tamm [3]. The lengthening of the halogen–gold bonds between FAuC and IAuC correlates well with the decrease in the magnitude of the natural charge on the halogen, decreasing the electrostatic interaction.

4. Summary

The molecular spectroscopic properties and thermochemistry of the XAuC (X = F, Cl, Br, I) series of molecules and their related diatomic gold carbides and halides have been accurately investigated using the CCSD(T) method with systematic treatments of basis set truncation errors, core–valence correlation, and scalar and spin–orbit relativistic effects. Where available the present results are in excellent agreement with experiment. The results on the XAuC species indicate that

partial multiple bonds characterize their molecular structures with FAuC predicted to have one of the shortest bonds involving gold in a neutral molecule. In regards to the thermochemistry of these species, the Au–C bond in FAuC has a predicted dissociation energy larger than any other neutral gold species. In general, the CCSD(T) dissociation energies obtained in this work are estimated to be accurate to within about 1–2 kcal/mol, which may represent the most accurate estimates of the dissociation energies of any of these species. Better error estimates would require more extensive experimental thermochemical data with which to compare to. In particular though, it appears from the present work on the gold halides that spectroscopic constants of a high accuracy similar to those obtainable for molecules containing only light elements is achievable for heavy-element containing molecules with the use of accurate relativistic pseudopotentials, as long as the effects of basis set truncation, correlation of semi-core electrons, and spin–orbit coupling are accurately taken into account.

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