Journal of Molecular Structure: THEOCHEM 955 (2010) 71–74

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

Theoretical study of the interaction between Au(I) and I on the $[AuI_2]^-$–I_2 complexes

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ARTICLE INFO

Article history:
Received 5 May 2010
Received in revised form 26 May 2010
Accepted 30 May 2010
Available online 4 June 2010

Keywords:
Second interaction
Gold(I)
Iodine

ABSTRACT

We studied the interaction between $[AuI_2]^-$ and I_2 using ab initio methodology. We found that the changes around the equilibrium intermolecular distance $Au\cdots I_2$ and in the interaction energy differences are sensitive to the electron correlation potential. We evaluated these effects using several levels of theory, including MP2, MP4 and CCSD(T); and size of the basis set on atoms. The equilibrium distances Au–I_2 in the complexes are in the range 380–392 pm. The obtained interaction energies differences at the equilibrium distance range from 4.3 to 14.7 kJ/mol at the different levels used. These results indicate that the complexes formed are in the category of van der Waals systems. At long-distances, the behaviour of the $[AuI_2]^-\cdots I_2$ interaction may be related mainly to charge-induced dipole and dispersion terms. Both terms are important.

1. Introduction

In recent years, the bonding interaction between closed-shell systems has been widely studied from the theoretical and experimental viewpoints [1,2]. Non-covalent interactions range from extremely weak van der Waals forces to metallophilic and extremely strong interactions [3–5]. Among the systems that we have studied, two complementary forces have been identified: charge-induced dipole (cid) and dispersion (disp) interactions. For example, in the systems $[Pt(PH_3)_3–Tl]^+$, $[AuCl(PH_3)_2–Tl]^+$, $[C_2H_4–Tl]^+$, $[C_2H_2–Tl]^+$ and $[Pt(PH_3)_3–Au]^-$ [6–9] the largest contribution to the total energy is due to the charge-induced dipole interaction term [10], but dispersion effects acquire significance near the equilibrium bond lengths. On the other hand, when the systems are neutral, the dispersion term is found as the principal contribution to the stability, such as in the $[Pt(PH_3)_3–Hg]$, [Au–CO] and $[Au–C_2H_4]$ [9,11,12] complexes.

Gold(I) iodides are well known to establish interactions described as van der Waals or closed-shell type [13]. Quantum chemical calculations indicate that the chemical bonding in the secondary-bond region (between 300 and 400 pm) can be very adequately described in terms of weak covalent bonding such as $[AuI_2{}^-]–I_2$ and $I_2–[Au_2I_2]–I_2$ [14,15]. For the first system, calculation at the MP2 level displays a minimum corresponding to the bent L-shape [14]. The interaction occurs through the iodides. For the second system, $I_2–[Au_2I_2]–I_2$, there are weak interactions between the I_2 molecule and one gold of the fragment Au_2I_2 [15]. The distance from one gold atom to the center of I_2 is 321.6 pm. The interaction energy between I_2 and Au_2I_2 at the MP2 level is indeed weak: 87.1 kJ/mol. Moreover, it has been published dissociation energy calculations of $[AuI_4]^-$ to $[AuI_2]^-$ and I_2. Schwerdtfeger and co-workers concluded “electron correlation as well as relativistic effects play a very important role in the decomposition reaction” [16].

Considering that gold has greatly attracted the attention of the scientific community due to the remarkably strong effects of relativity on it, which results in an element with an expanded *d* shell, and hence high polarizability and proneness to closed-shell interactions [17,18], we have found it interesting to analyze theoretically the interaction between the anionic gold iodide complex $[AuI_2]^-$ and I_2 through the central gold atom and the molecule of iodine.

The aim of the present work is to study theoretically the intermolecular closed-shell interaction using $[AuI_2]^-\cdots I_2$ as a model, comparing the $Au\cdots I$ distances, and estimating the strength of this interaction at the MP2, MP4 and CCSD(T) levels using scalar relativistic pseudopotentials (PPs). Unlike the previous study with a bent L-shape, we focus on the hypothetical structure where there is direct interaction between gold and iodine. To understand the nature of the interaction in study, we made use of two simple expressions for charge-induced dipole and dispersion terms estimated from the individual properties of $[AuI_2]^-$ and I_2 at the MP2 level [10]. These expressions have been successfully used in previous work from our group [6–9].

2. Models and computational details

The $[AuI_2]^-\cdots I_2$ model is depicted in Fig. 1. The model assumes a C_2 point symmetry. The calculations were made with Gaussian 03 [19] using two different basis sets. The smaller set (VDZP) consists

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doi:10.1016/j.theochem.2010.05.033

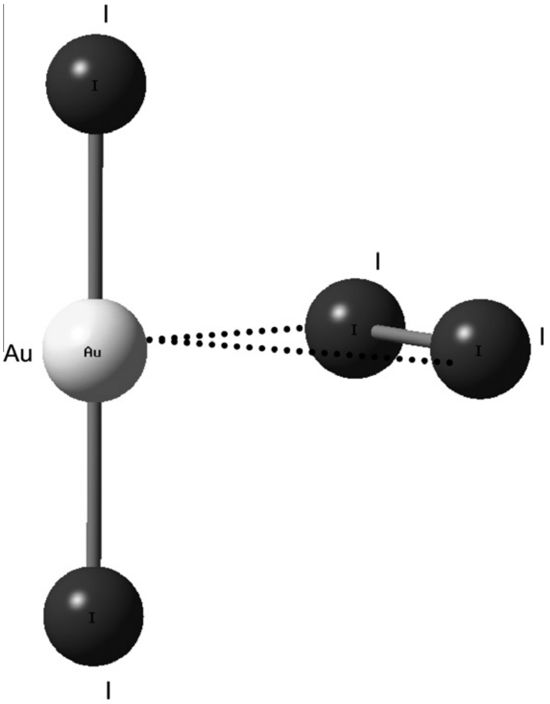

Fig. 1. Model of the $[AuI_2]^{-}\cdots I_2$ system.

Table 1
Main geometric parameters of the $[AuI_2]^{-}\cdots I_2$ system (distances in pm and angles in degrees) at different levels of calculation. The interaction energy $V(R_e)$ is shown with BSSE and in parentheses without BSSE (kJ/mol).

Method	IAu[c]	I–I	IAuI[c]	Au···I[d]	IXAuI[e]	$V(R_e)$
MP2[a]	258.0	270.9	180.0°	379.6	90.0°	−9.2 (−31.7)
MP2[b]	253.7	265.5	180.0°	370.3	89.8°	−14.7 (−36.9)
MP4[a]	260.4	274.1	180.0°	386.5	90.2°	−6.6 (−29.3)
MP4[b]	256.4	268.0	180.0°	375.5	89.8°	−11.3 (−34.3)
CCSD(T)[a]	262.3	274.5	180.0°	392.9	90.0°	−4.3 (−25.7)
CCSD(T)[b]	258.2	268.5	180.0°	386.2	89.9°	−7.3 (−28.2)

[a] Basis set 1.
[b] Basis set 2.
[c] Intramolecular distance in $[AuI_2]^{-}$ system.
[d] Intermolecular distance in $[AuI_2]^{-}\cdots I_2$.
[e] Dihedral angle. X is middle position among iodines in I_2.

Table 2
NBO analysis of the MP2, MP4 and CCSD(T) densities for $[AuI_2]^{-}\cdots I_2$.

Method	Charge	Electron configuration
MP2[a]		
Au	+0.36	$[core]6s^{0.73}\ 5d^{9.87}\ 6p^{0.08}\ 7s^{0.01}$
I[c]	−0.68	$[core]5s^{1.94}\ 5p^{5.53}\ 5d^{0.10}\ 6p^{0.02}$
I[d]	+0.01	$[core]5s^{1.94}\ 5p^{4.95}\ 5d^{0.09}\ 6p^{0.01}$
MP2[b]		
Au	+0.36	$[core]6s^{0.73}\ 5d^{9.87}\ 6p^{0.08}\ 7s^{0.01}$
I[c]	−0.68	$[core]5s^{1.94}\ 5p^{5.73}\ 5d^{0.10}$
I[d]	0.00	$[core]5s^{1.94}\ 5p^{5.02}\ 5d^{0.01}\ 6p^{0.01}$
MP4[a]		
Au	+0.39	$[core]6s^{0.69}\ 5d^{9.88}\ 6p^{0.01}$
I[c]	−0.70	$[core]5s^{1.95}\ 5p^{5.74}\ 5d^{0.01}$
I[d]	0.00	$[core]5s^{1.95}\ 5p^{5.02}\ 5d^{0.01}$
MP4[b]		
Au	+0.37	$[core]6s^{0.72}\ 5d^{9.87}$
I[c]	−0.69	$[core]5s^{1.94}\ 5p^{5.73}\ 5d^{0.01}$
I[d]	0.00	$[core]5s^{1.95}\ 5p^{5.02}\ 5d^{0.01}$
CCSD(T)[a]		
Au	+0.40	$[core]6s^{0.68}\ 5d^{9.89}\ 6p^{0.01}$
I[c]	−0.70	$[core]5s^{1.95}\ 5p^{5.74}\ 5d^{0.01}$
I[d]	0.00	$[core]5s^{1.95}\ 5p^{5.02}\ 5d^{0.01}$
CCSD(T)[b]		
Au	+0.38	$[core]6s^{0.71}\ 5d^{9.87}$
I[c]	−0.69	$[core]5s^{1.94}\ 5p^{5.73}\ 5d^{0.01}$
I[d]	0.00	$[core]5s^{1.95}\ 5p^{5.02}\ 5d^{0.01}$

[a] Basis set 1.
[b] Basis set 2.
[c] Iodine in $[AuI_2]^{-}$ system.
[d] Iodine in I_2 molecule.

of an energy-consistent quasirelativistic (QR) 19-valence-electron (VE) pseudopotential (PP) and an (8s7p6d2f)/[7s6p3d2f] valence basis set for gold [20]. For the iodine atom use has been made of 7-VE PPs with the corresponding VDZP basis set adding one *d*-type polarization function (4s5p2d)/[2s3p2d] [21]. We called these sets "basis set 1".

As the large basis set (AVTZ) an uncontracted (8s7p6d3f2g)/[7s6p3d3f2g] valence basis set was used for the 19-VE gold. The augmented (3f2g) functions were identical to those used in the QR case [20]. For iodine use was made of one *d*- and *f*-type functions: (4s5p3d1f)/[2s3p3d1f]. We called these sets "basis set 2".

The Au···I intermolecular interaction energy was obtained using each of the wing methods: MP2, MP4 and CCSD(T). Although the computational methodologies do not consider spin–orbit interactions, the complex under investigation is a closed-shell singlet, so they should have only minor importance. The counterpoise correction for the basis set superposition error (BSSE) was used for the calculated interaction energies. We have fully optimized the geometry of the model for each one of the methods mentioned above. Although it is known that the MP2 approximation exaggerates the attractive interactions, this method gives a good indication of the existence of van der Waals interactions [22,23].

3. Results and discussion

Table 1 summarizes the main geometric parameters and interaction energies obtained for the model system at different levels of the calculations. In this section, we will discuss the Au···I geometries and interaction energies in the complexes. The natural bond orbital (NBO) [24] analysis is given in Table 2. Finally, the origin of the intermolecular interactions will be studied as simple inductive and dispersion expressions obtained for the individual properties of the $[AuI_2]^{-}$ complex and I_2 diatomic molecule.

3.1. Short-distance behaviour

The results of the calculations (see Table 1) support the originally proposed idea, i.e., that the $[AuI_2]^{-}\cdots I_2$ systems show van der Waals type closed-shell interactions. Concerning the Au···I intermolecular distances and the interaction energies, it is clear that the electronic correlation effects play an important role in the stability of the systems. At the HF level there is no minimum interaction energy. The Au···I intermolecular distances obtained with all the methods show variations; when going from MP2 to CCSD(T) an increase of the Au–I distance occurs. Similarly, when going from "basis set 1" to "basis set 2", there is a decrease of that distance. It is possible to see the effect of the increased size of the basis set (See Fig. 2).

The magnitude of the interaction energies obtained varies according to the method used: between 9.2 kJ/mol (MP2) and 4.3 kJ/mol (CCSD(T)) for "basis set 1", and between 14.7 kJ/mol (MP2) and 7.3 kJ/mol (CCSD(T)) for "basis set 2". The effect of working with a larger base is seen in an increase in the magnitude of the interaction energy. However, as seen in Table 1, the interaction energies without BSSE are largely overestimated. When the