Explaining the magnetism of gold

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Abstract In the present work, a computational study is performed in order to clarify the possible magnetic nature of gold. For such purpose, gas phase Au_2 (zero charge) is modelled, in order to calculate its gas phase formation enthalpy. The calculated values were compared with the experimental value obtained by means of Knudsen effusion mass spectrometric studies. Based on the obtained formation enthalpy values for Au_2, the compound with two unpaired electrons is the most probable one. The calculated ionization energy of modelled Au_2 with two unpaired electrons is 8.94 eV and with zero unpaired electrons, 11.42 eV. The difference (11.42-8.94 = 2.48 eV = 239.29 $kJmol^{-1}$), is in very good agreement with the experimental value of 226.2 ± 0.5 $kJmol^{-1}$ to the Au-Au bond. So, as expected, in the specie with none unpaired electrons, the two $6s^1$ (one of each gold atom) are paired, forming a chemical bond with bond order 1. On the other hand, in Au_2 with two unpaired electrons, the s-d hybridization prevails, because the relativistic contributions. A molecular orbital energy diagram for gas phase Au_2 is proposed, explaining its paramagnetism (and, by extension, the paramagnetism of gold clusters and nanoparticles).

Keywords Gold, thermochemistry, Au_2, paramagnetism, formation enthalpy, energy diagram

Introduction

Despite a study about induced paramagnetism on gold [1], bulk gold (Z= 79; electron configuration $[xe]\, 4f^{14}5d^{10}6s^1$) is known to be a typical diamagnetic material. Magnetic properties of gold nanoparticles and clusters have been reported [2]. However, some results are contradictory, and a clear understanding of this phenomenon is still missing. Apparently, as one pass from bulky solid gold to gold nanoparticles or clusters, the unpairing of electrons takes place. In this connection, to model gas phase gold could be a key procedure to clarify the claimed gold magnetism.

As shown to PtF_6 [3], thermochemical data can be of paramount importance to a fully understanding of the magnetic properties of inorganic compounds.

In the present work, a computational study is performed in order to clarify the possible magnetic nature of gold. For such purpose, gas phase Au_2 (zero charge) is modelled, in order to calculate its gas phase formation enthalpy.

Methodology

All computations were performed by using Spartan´16 [4]. Thermochemical calculations were performed by semi-empirical (PM6) method. The SE-PM6 approach was chose taking into account its minor computation time consuming and its reliability, as verified for PtF_6 [3]. The calculated values were compared with the experimental value obtained by means of Knudsen effusion mass spectrometric studies [5].

Results and Discussion

The obtained results are summarized in Table 1.As can be verified, based on the obtained formation enthalpy values for Au_2, the compound with two unpaired electrons is the most probable one.

So, is concluded here that gas phase Au_2 is paramagnetic, with two unpaired electrons (and so, with a calculated spin only magnetic moment of 2.83 BM). So far the author is concerned; there are not, in the literature, magnetic moment measurements for gas phase Au_2. Nevertheless, a magnetic moment of 2.36 BM per particle was reported [6] for deposited gold nanoparticles. It was verified that the magnetic contribution originates at the particle's Au 5d band [6].

Table 1: Calculated and experimental gas phase formation enthalpy ($kJmol^{-1}$) values for Au_2 [5]

$\Delta_g H_f^0$ (exp)	$\Delta_g H_f^0$ (calc.)	
509.96 ± 4.18^a	Zero unpaired e^-	354.63
	Two unpaired e^-	584.28

The modelled Au_2 with zero unpaired electrons has an Au-Au distance of 223.8 pm, whereas for two unpaired electrons Au_2, the same bond has a 270.2 pm value. It is worth noting that the mean value, 247.0 pm, is in very good agreement with the reported experimental value [7] of 247.19 pm.

Hence, is concluded that in bulk gold, the $6s^1$ electrons are paired. However, in the gas phase, or even in gold clusters or gold nanometric particles, the unpairing of electrons turns easier. For comparison, the (first) ionization energy of gold is 9.23 eV [8]. The calculated ionization energy of modelled Au_2 with two unpaired electrons is 8.94 eV and with zero unpaired eletrons, 11.42 eV. The difference (11.42-8.94 = 2.48 eV = 239.29 $kJmol^{-1}$), is in very good agreement with the experimental value of 226.2 ± 0.5 $kJmol^{-1}$ to the Au-Au bond [7].

The calculated 8.94 values is in very good agreement with another calculated ones [9] by DFT: 8.789 eV and 8.960 eV by CCSD and CCSD(T) methods, respectively, showing that the choice of a SE method was a good one.

Hence, as expected, in the specie with none unpaired electrons, the two $6s^1$ (one of each gold atom) are paired, forming a chemical bond with bond order 1. The proposed molecular orbital energy diagram is shown in Figure 1.

It could be concluded that in gas phase Au_2, the $6s^1$ electrons are unpaired, and such fact can only be explained by saying that, from a thermodynamic point of view, the Au-Au system with two unpaired electrons (paramagnetic, of course) is more stable than the system with none unpaired electrons.
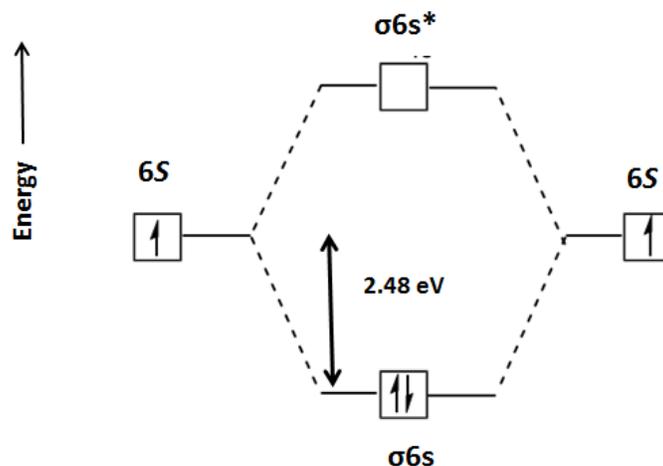
Figure 1: Proposed molecular orbital energy diagram for Au₂ (assuming no hybridization with d orbitals)

As is well known, gold, as well as another heavy and superheavy elements, have their properties largely influenced by relativistic contributions [10]. Gold, indeed, is, proportionally, the element of periodic table with the large percentage relativistic contraction, with a remarkable effect on its atomic energy levels, such as illustrated in Figure 2.

Taking into account the relativistic contraction, the $6s$ and $5d$ orbitals are closer, and a s-d hybridizations is feasible [11]. For convenience, Au_2 will be considered, in the proposed molecular orbital diagram shown in Figure 3, as formed by Au^- and Au^+. For convention, the d orbital involved in the hybridization is the orbital d_z^2 (hence, only σ bonds are formed) and the other d orbitals (not involved in the hybridization) are omitted from the proposed diagram.

The molecular orbital diagram in Figure 1 explains the diamagnetism of bulky gold, whereas the diagram in Figure 3 explains the paramagnetism of gas phase Au_2 (and, by extension, the paramagnetism of gold clusters and nanoparticles).
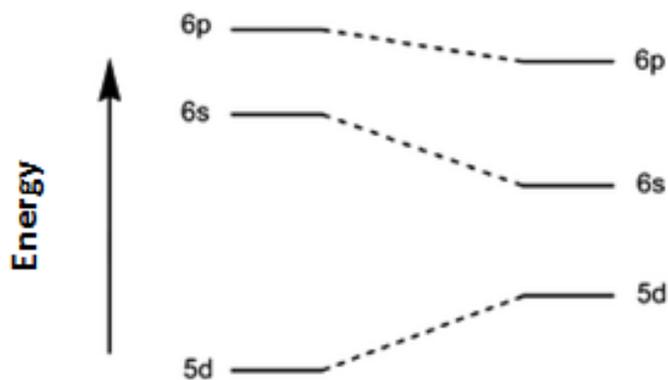
Figure 2: Relative atomic orbitals energy levels for gold: non-relativistic (left) and relativistic (right)
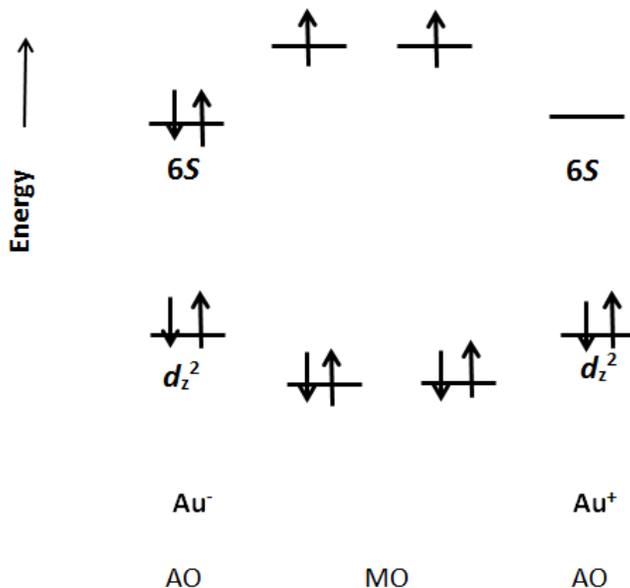
Figure 3: Proposed molecular orbital energy diagram for gas phase Au_2, explaining the presence of two unpaired electrons

As an inevitable conclusion, can be stated that only for gas phase (or clusters, or nanoparticles) the s-d hybridization prevails, explaining why, for bulk gold, paramagnetism is not observed. It is also possible to propose that the s-d hybridization facility (and, hence, magnetic properties) decreasing order is: gas phase → cluster → nanoparticle → bulk.

Such fact could be explained remembering that is the gas phase Au_2 energy levels resembles those for free gold atoms, whereas in a bulk sample (despite the fact that the conduction band is a s-d mixture [12]), the percentage of *d* character in the hybrid orbitals could be lower than in the gas phase.

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