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Theoretical studies of magnetic interaction in π-radical thiol and Gold hybrid systems

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Abstract

Nanoscale magnetic material is becoming an important topic in nanoscience and magnetism. Especially, gold nanoparticles chemisorbed by alkanethiols have drawn much attention due to the size effect on their electronic structure. However, magnetic interaction of gold nanoparticles derivatized by magnetically active ligands has not been investigated in detail. In order to elucidate the magnetic interaction in gold nanoparticles chemisorbed by alkanethiol systems, small gold cluster and π-radical hybrid model systems were examined using the hybrid DFT method. In this research, the effective exchange integrals (J_{ab}) of model systems were calculated for qualitative understanding of the intramolecular magnetic interaction. From these calculations, it was found that there was a possibility of controlling the magnetic interaction of these hybrid model systems using electron/hole doping.

Keywords: Ab initio quantum chemical methods and calculations, Density functional calculation, Models of surface and interface chemistry and physics, Heterojunction

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1. Introduction

The development of nanostructured magnetic materials with a characteristic electronic structure is an urgent requirement in spintronics. In this regard the combination of Au and organic radicals forms an interesting material, because the relationship between the conduction electron of Au and the isolated spin of the organic stable radicals shows a unique magnetic interaction. This hybrid material, which is composed of an Au cluster and a stable organic radical molecule, was actually presented by Izuoka et al. and showed a paramagnetic spin order [1].

Considering their physical and chemical properties, nanosized materials are surprisingly different from bulk materials. For example, although bulk Au is chemically inactive, when deposited as nanoparticles on select metal oxides it shows high catalytic activity for CO oxidation at room temperature [2–7]. This catalytic activity of Au nanoparticle deposited catalyst is mainly due to the size of each Au nanoparticle and the hetero-junction between Au particle and the selected metal oxide support [9, 8]. The hetro-junction effect of Au catalyst is presumed to be caused by the electronic state between the interface Au atoms of Au nanoparticles and the support being modified by charge transfer between them. This suggests that the change in the electronic state of Au affects the characteristics of Au.

Change in the magnetic interaction of organic radicals by hole/electron doping was successfully proposed in the 1980's [10, 11]. It was hypothesized that hole/electron doping could be a key factor in creating a nanospin material that has spin crossover between ferro- and antiferromagnetic interaction, because modification of the electronic state of the Au nanocluster by electron/hole doping might have an effect on the magnetic interaction of the hybrid material, which is composed of Au clusters and organic spin molecules. To elucidate this hypothesis, *ab initio* calculations for the model hybrid systems were carried out.

2. Calculation method and models

2.1 *Calculation method*

All computations were performed using the GAUSSIAN

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98 program package [12]. Unrestricted hybrid DFT (UB3LYP) was applied for the model system computations, with the D95** basis set used for C, N, O, and H and the LANL2DZ basis set used for Au.

The low spin state and high spin state (LS-HS) energy gap of the systems was experimentally determined using the Heisenberg (HB) Hamiltonian. The effective exchange integrals (J_{ab}) can also be calculated using combinations of the spin-polarized DFT energies with the Heisenberg model as follows [6, 13, 14].

$$J_{ab} = \frac{(E(LS) - E(HS)}{(\langle S^2 \rangle (HS) - \langle S^2 \rangle (LS))} \qquad (1)$$

2.2 Calculated models

In the real system, π-radical thiols that are a phenyl sulfide derivative (SPN-hex) were chemisorbed onto Au nanoparticles whose mean diameter was approx. 4 nm. The obtained hybrid system was named SPN-hex@Au. The schematic diagram of this real system is shown in Figure 1. From detailed analysis the representative chemical formula was determined to be $Au_{1750}(SPN\text{-}hex)_{125}$.

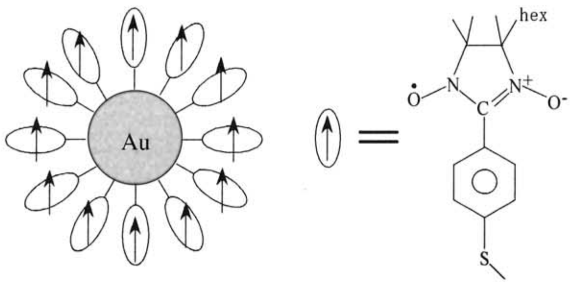

Fig. 1. Schematic diagram of SPN-hex@Au system.

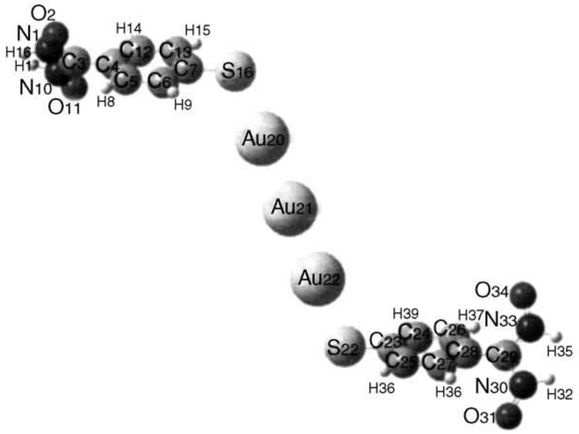

Fig. 2. Illustration of the Au-organic spin molecule hybrid model system.

It would be difficult to examine this real system using the *ab initio* method with current computer resources. However, because our interest is focused on the effects of electron/hole doping of the metal-organic hybrid system, a smaller model system is feasible for the elucidation of this subject. Hence the small model system shown in Figure 2 was adopted. Here the wire-like Au_3 cluster is used instead of a large Au cluster and the SPN-hex is modified to phenyl sulfide with a simple nitronyl nitroxide group. The geometry of the organic spin molecule was based on the geometry of an NPNN molecule.

3. Results and Discussion

Initially a neutral cluster was examined. The results obtained are shown in Table 1. The ground state of the neutral cluster was a doublet state. Because the effective exchange integral of this cluster was -2076 cm^{-1}, it was determined that the magnetic interaction was antiferromagnetic. The spin angular moments of the model systems are shown in Table 2. (Note that only the spin densities of the heavy atoms are summarized in this table.) From calculation of the organic radical fragment, it was determined that the ground state of the fragment was a triplet state. For the doublet state of the neutral hybrid model system, the opposite sign of the spin moments were presented on the S atoms. This result suggests that the hetero-junction between the Au cluster and the stable organic spin molecules has an effect on the spin alignment of the hybrid model system. Considering surface adsorption, it could be said that this spin alternation is mainly due to the charge transfer between Au and S atoms.

The effects of electron doping of this model system were then examined. The calculated results suggested that the low spin state was still the ground state, as the obtained ground state was a singlet state. However, the LS-HS energy gap of this system was extremely decreased.

Table 1
Total energies, total spin angular moments and effective exchange integrals (cm^{-1}) for the model hybrid systems

Charge	Spin State	Energy/ hr	S**2	J/ cm^{-1}
Neutral[1]	doublet	-2263.19954534	1.8986	
	quintet	-2263.17122532	4.8929	-2076
Anion[1]	singlet	-2263.36303232	1.2196	
	triplet	-2263.36302790	2.1834	-1.01
Cation[1]	singlet	-2262.93828722	1.4348	
	triplet	-2262.93878147	2.2495	133.2

1) UB3LYP/LANL2DZ was used for Au and D95** for others.

The charge distribution and spin moment analyses showed that the doped electron was mainly localized on an Au cluster site and the spin moments of Au cluster sites were greatly decreased.

With hole doping, it was found that the high spin state