

^{13}C chemical shifts in octanethiols adsorbed on gold: a theoretical study[☆]

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Received 21 February 2001; accepted 3 March 2001

Abstract

Clusters consisting of $[\text{Au}_3\text{SC}_8\text{H}_{17}]^{2+}$ and $[\text{Au}_5\text{Cl}_4\text{SC}_8\text{H}_{17}]$ are employed in ab initio shielding calculations to model octanethiols adsorbed on the surface of gold nanoparticles. The isotropic shielding and its principal components are calculated using the coupled Hartree–Fock gauge-including atomic orbital (CHF-GIAO) method. The computed values compare favorably with those observed in solid state nuclear magnetic resonance (NMR) measurements of octanethiol-coated gold nanoparticles. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Au nanoparticles; Octanethiol; ^{13}C NMR chemical shifts

1. Introduction

As research on surface-modified gold nanoparticles become increasingly attractive due to their potential applications [1–8], it has become imperative to utilize the most commonly used organic structural tool, nuclear magnetic resonance (NMR) spectroscopy, to understand on a molecular level the bonding between the organic substrate and the gold nanoparticle. Previous NMR measurements [9–15], performed in both solution and solid-state, have demonstrated the feasibility of observing resonances arising from the nuclei in an alkyl thiol chain bound to a gold surface. Unfortunately, broadening of resonances of both ^1H and ^{13}C nuclei that reside in proximity to the gold

surface, has precluded the precise measurement of their chemical shifts. As Badia et al. [10] pointed out, the broadening of the resonances of the nuclei close to sulfur is primarily due to a distribution of shifts. The NMR chemical shift is very sensitive to local structure and differences in adsorption sites can easily lead to varying shifts. Due to this distribution of shifts, the lines become inhomogeneously broadened that they disappear under the baseline. Previous NMR measurements [9,10] indicate that this is the only stumbling block as longitudinal measurements demonstrate motions along the octyl chain suitable for seeing well-resolved signals, and hole-burning experiments indicate that the broadening is inhomogeneous. These studies have shown that metallic contributions in the form of Knight shifts to the observed resonances are negligible.

Methods of computing shielding have reached a stage at which the quality of the calculated numbers has already approached the precision of the experiment [16]. As an example, Rich et al. [17] have

[☆] Dedicated to Professor Graham A. Webb on the occasion of his 65th birthday.

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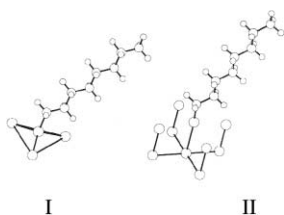


Fig. 1. Optimized structures employed in this work: **I** ($\text{Au}_3\text{SC}_8\text{H}_{17}$)²⁺ and **II** ($\text{Au}_5\text{Cl}_4\text{SC}_8\text{H}_{17}$).

shown that *ab initio* calculations can reproduce even the subtle differences between the shielding tensors of methyl carbons in the two antibiotics, penicillin-V and ampicillin. Anisotropy differences in the order of 1 ppm are nicely predicted by theory in these two antibiotics. At this level of accuracy and with the assumption that the conduction electrons in the gold core do not contribute to the chemical shifts of the octyl chain, *ab initio* shielding computations may help elucidate or interpret NMR data on octanethiol-coated gold nanoparticles.

Beardmore et al. [18] have shown through *ab initio* computations that the potential function describing the interaction between an alkanethiol chain and a gold surface is generally flat with respect to lateral motion. A barrier of only 1 kcal/mole is predicted for the motion of the headgroup between hollow sites on a Au(111) surface. Thus, for a surface that has less than a full monolayer coverage, it is very likely that the thiols are moving between sites. To map the potential surface, Beardmore et al. [18] have utilized a cluster consisting of 17 Au atoms. Ten of these Au atoms define the surface while the remaining seven are in a second layer. Smaller clusters involving 9 Au atoms have also been shown to yield very similar energies and equilibrium structures.

This paper will employ presently available methods for shielding computations. A closed shell electronic configuration will be assumed by incorporating only surface Au atoms, each one bearing an oxidation state of one. Two configurations will be examined. First, the thiol S atom will be placed at a 3-fold hollow site. In a second configuration, the S atom will be lying on top of a gold atom. It is hoped that these calculations will reveal the expected shielding range for the atoms near the S. Since the computations will likewise yield the complete tensor information, the magnitude of the

principal components as well their orientations will be reported.

2. Computational details

Both geometry optimization and shielding computation are performed using a parallel version of GAUSSIAN 98 [19]. The clusters used in the calculations are shown in Fig. 1. To mimic a hollow site, a model cluster of formula $[\text{Au}_3\text{SC}_8\text{H}_{17}]^{2+}$ (**I**) is employed. In this structure, the S atom resides on the threefold axis defined by the three Au atoms. The second cluster, $[\text{Au}_5\text{Cl}_4\text{SC}_8\text{H}_{17}]$ (**II**), as shown in Fig. 1, contains a S atom placed on top of a Au atom residing at the center of a square defined by four additional Au atoms. To minimize the charge of the cluster, four Cl ions are added, one on top of each corner Au atom. The atoms that belong to octanethiol are assigned standard 6-311 + G(1d,1p) basis sets while Au and Cl are assigned LANL1MB effective core potentials [20], where only the valence shell electrons are represented explicitly with a minimum basis set. Both clusters are subjected to geometry optimization with the following restrictions. For **I**, the threefold axis defined by the Au atoms is kept and the S atom is restrained to stay along this axis. For **II**, the fourfold axis defined by the four corner Au atoms is maintained and both the central Au and the thiol S atoms are forced to remain along this axis. Only these symmetry restraints are imposed, thus, the Au atoms are also allowed to relax, as long as they stay at the corners of an equilateral triangle, in the case of **I**, and at the corners of a square, in the case of **II**. The optimization is performed at the B3LYP (a hybrid method which makes use of the Becke exchange functional [21] mixed with Hartree–Fock contributions and the correlation functionals of Lee et al. [22]) level of theory. The structures shown in Fig. 1 are the results of the geometry optimizations. Using the optimized structures, the NMR shieldings are calculated via the gauge-including atomic orbital (GIAO) method [23,24] at the restricted Hartree–Fock (RHF) level of theory. These calculations were performed on an Origin 2000 Workstation equipped with four processors (Silicon Graphics, Inc.). For comparison, corresponding calculations are likewise performed on a gold thiolate complex, $\text{AuSC}_8\text{H}_{17}$. Computational times ranged from 1 to 2 days.

Table 1

Calculated principal values of ^{13}C chemical shift tensors in $[\text{Au}_3\text{SC}_8\text{H}_{17}]^{2+}$ (**I**)

Nucleus	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
C ₁	82.7	49.0	5.7
C ₂	107.0	53.7	− 3.4
C ₃	56.4	31.3	7.4
C ₄	52.7	35.6	7.3
C ₅	49.3	33.8	8.2
C ₆	51.0	36.5	8.6
C ₇	36.1	25.9	10.1
C ₈	25.5	20.4	− 1.2

Table 3

Calculated principal values of ^{13}C chemical shift tensors in $[\text{AuSC}_8\text{H}_{17}]$

Nucleus	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
C ₁	62.8	19.5	9.9
C ₂	104.6	46.3	3.1
C ₃	54.3	31.1	9.5
C ₄	52.8	32.7	10.0
C ₅	50.4	32.0	10.6
C ₆	52.6	34.3	10.8
C ₇	35.9	24.4	11.2
C ₈	26.6	20.5	− 2.4

3. Results and discussion

The optimized structures differ slightly from those of Beardmore et al. [18]. In **I**, the Au–S distance is 2.6 Å, while in **II**, it is 3.1 Å. These distances are about 0.3 Å larger than those of previous work [18]. These differences are only expected since the models used in this present work lack a second layer of Au atoms. In the geometry optimization step, the Au atoms are allowed to relax, which leads to an increase in the Au–Au distances. The monomeric gold-thiolate ($\text{AuSC}_8\text{H}_{17}$) complex structure derived from this present work exhibits a Au–S distance of 2.5 Å, a Au–S–C₁ angle of 102°, and a S–C₁ length of 1.8 Å.

Here are some details describing the optimized structures obtained for **I** and **II**. In both cases, the S–C₁ bond lies almost normal to the plane defined by the Au atoms, deviating by only 9° in **I** and 6° in **II**. The two structures shown in Fig. 1 also display small differences in the S–C₁ bond length, 1.9 Å (**I**) and 1.8 Å (**II**), and in the C₁–C₂ bond length, 1.52 Å (**I**) and 1.55 Å (**II**). With these differences in mind, it

is expected that the shielding values of C₁ and C₂ will vary between **I** and **II**. The computed ^{13}C chemical shift tensor components are presented in Tables 1 and 2. The calculated ^{13}C principal components for the gold thiolate complex are shown in Table 3. For comparison, experimental isotropic shifts taken from Badia et al. [9,10] are displayed with the calculated isotropic shifts in Table 4. These experimental values combine chemical shifts measured for $\text{C}_8\text{H}_{17}\text{SAu}$ and $\text{C}_{14}\text{H}_{29}\text{SAu}$ nanoparticles. Specifically, the chemical shifts attributed to C₁ and C₂ are those observed in $^{13}\text{C}_1\text{–AuSC}_{14}$ and $^{13}\text{C}_2\text{–AuSC}_{14}$ nanoparticles [10], respectively, while the rest are taken from measurements involving octanethiol-coated Au nanoparticles [9]. The calculated absolute shielding values have been converted to chemical shift values (reference is tetramethylsilane) by setting the isotropic chemical shift of C₈ to equal exactly 14.9 ppm.

The values presented in Tables 1–3 indicate that the shielding tensors of C₁, C₂, and C₃ are sensitive to the presence of Au atoms, with C₃ being only mildly influenced. C₄, C₅, and C₆ exhibit principal

Table 2

Calculated principal values of ^{13}C chemical shift tensors in $[\text{Au}_5\text{Cl}_4\text{SC}_8\text{H}_{17}]$ (**II**)

Nucleus	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
C ₁	144.2	27.7	− 63.2
C ₂	52.3	32.5	6.1
C ₃	49.2	37.4	2.9
C ₄	48.0	32.9	7.7
C ₅	50.3	33.1	9.1
C ₆	51.9	34.7	10.0
C ₇	36.1	25.1	10.7
C ₈	26.6	20.8	− 2.7

Table 4

Isotropic ^{13}C chemical shifts

Nucleus	I	II	$\text{AuSC}_8\text{H}_{17}$	Experiment ^a
C ₁	45.8	35.7	30.8	42
C ₂	52.5	30.5	51.3	46
C ₃	31.7	29.8	31.6	
C ₄	31.9	29.5	31.8	31.1
C ₅	30.4	30.9	31.0	31.1
C ₆	32.0	32.2	32.6	33.1
C ₇	24.0	24.0	23.8	23.8
C ₈	14.9	14.9	14.9	14.9

^a From Refs. [9,10].

shift components typical of methylene carbons in an alkyl chain, while C_7 represents a methylene carbon attach to a terminal methyl group. In fact, the isotropic value as well as the principal components of the ^{13}C chemical shifts for C_4 – C_8 in **I** and **II** are indeed very similar between these two model systems. The calculated chemical shift components for C_1 in the monomeric gold-thiolate complex differ substantially from those of **I** and **II**. In the absence of other Au atoms, the C_1 site appears to be more shielded. Interestingly, Au(I) thiolates are rarely observed as monomers, instead, this compound usually forms linear polymeric or ring structures, with Au being doubly coordinated [25]. Hence, the calculated chemical shifts of gold thiolate do not compare favorably with those observed in Au(I) thiolates [10]. Clearly, the presence of other Au atoms contributes significantly to the chemical shifts of both C_1 and C_2 .

In the free thiol, C_1 (24.5 ppm from TMS) is more shielded than any of the carbons, except for C_7 and C_8 [9]. C_2 (33.9 ppm), on the other hand, is the most deshielded nucleus in the free octanethiol. C_3 (28.2 ppm) in the free thiol can still be resolved from the other methylene carbons C_4 and C_5 (29.0 ppm). For both **I** and **II**, it is evident that the shielding at C_3 has become very close in value to those of C_4 and C_5 . In addition, the resonances for C_4 and C_5 will be slightly broadened due to the distribution of sites. Thus, in the one-dimensional ^{13}C spectrum of octanethiol-coated Au nanoparticles, the resonance due to C_3 has probably overlapped with the peak attributed to C_4 and C_5 .

The sites C_1 and C_2 are dramatically more different between **I** and **II**. The difference between the isotropic shifts of C_1 in **I** and **II** is about 10 ppm while for C_2 , the calculated change is more than 20 ppm. The observed linewidths for these sites are broader than the variations seen here. However, in the sample, there are other possible sites, as there are several face types expected to be present in the small Au particles. The results of the calculations illustrate that the isotropic chemical shifts of both C_1 and C_2 are indeed heavily influenced by the type of Au–S bonding. Spinning at the magic angle will not remove this inhomogeneity, thus, it is no surprise that the lines attributed to these sites are especially wide.

The calculated chemical shifts for C_1 and C_2 using model **I** agrees closest to experiment. The results even

indicate that C_2 is deshielded compared to C_1 , in agreement with experiment. This pattern is experimentally observed for thiolates while the opposite is observed for disulfides. The results of this work, however, do not agree with those predicted by Terill et al. [11], in which C_1 resonates at 27 ppm and C_2 is predicted to lie at 36 ppm. These predictions take into account only the magnetic susceptibility contribution. Clearly, the Au–S bonding contributes to the shifts of both C_1 and C_2 and the broadening is not due to dipolar broadening but to the particles being faceted. Lastly, since the experimental values [9,10] are closer to those obtained using model **I**, the calculations shown here suggest that most of the thiols are sitting on threefold hollow sites. This is likewise in agreement with the potential surface calculations of Beardmore et al. [18], which indicates that the three-fold hollow site is the energy favored adsorption site.

Both C_1 and C_2 shielding tensors exhibit a substantial span. From **I**, it seems that the component most sensitive to the Au–S bond is δ_{11} , the least shielded component. Compared to the other methylene carbons, the δ_{11} components of C_1 and C_2 are especially deshielded. This component lies perpendicular to the thiol long axis S–C bond. The intermediate component δ_{22} is also orthogonal to the S–C bonds and thus, appears to become deshielded like δ_{11} . The component that lies parallel to the S–C vector (δ_{33}) resembles those of the other methylene carbons. Interestingly, this orientation of the principal axis system corresponds to the calculated orientation in the monomeric gold-thiolate complex.

To illustrate further the orientation of the principal axes of the chemical shift tensors in these systems, the following frame is introduced. The direction normal to the plane defined by the Au atoms is designated the z axis. The plane containing the carbons on the octyl chain is the yz plane. In this frame, the octyl chain is leaning from the z axis such that its projection on the plane of the Au atoms (the xy plane) lies along the x axis. Incidentally, for both **I** and **II**, there exists a mirror plane which coincides with the xz plane in the frame described. With this laboratory frame, the least shielded component, δ_{11} , of all the carbon nuclei lies parallel to the y axis. For C_1 , δ_{22} is very close to the x -axis while δ_{33} is normal (z axis) to the plane defined by the Au atoms. This is true for both systems **I** and **II**. The orientation of the chemical shift tensor of

C₂ is very similar to those of C₁. However, as one goes farther along the alkyl chain, it appears that the most shielded component is in fact following the long axis of the octyl chain. The optimized structures (shown in Fig. 1) have octyl chains that are not exactly perpendicular to the plane of the Au atoms. In **I**, the long axis of the thiol molecule is about 35° from the normal direction while in **II**, the chain is about 20° from being normal. Consequently, for C₃–C₇, δ_{33} no longer lies exactly along the *z* axis. In fact, for these carbons in both **I** and **II**, the most shielded component lies almost parallel to the long axis of the thiol. The least shielded component in all of the carbon nuclei stays parallel to the *y* axis, normal to the plane defined by the octyl carbons.

If, in the future, NMR studies of a monolayer become feasible, these will most probably involve ¹H NMR measurements [26]. Thus, the calculated ¹H chemical shift tensors are discussed here briefly. The orientations of ¹H chemical shift tensors are not as straightforward to describe. The least shielded component, δ_{11} , of each of the proton lies nearest to its corresponding C–H vector. For the protons attached to C₁ in **I**, whose resonances are not observed in thiol-coated gold nanoparticles in solution, the calculated isotropic chemical shift is 3.0 ppm and the components are 11.3, 2.2, and –4.4 ppm. These calculated chemical shifts are obtained from the absolute shieldings after setting the methyl protons' value at 0.9 ppm (reference is tetramethylsilane). The most shielded component, –4.4 ppm, lies normal to the plane defined by the Au atoms. Calculations indicate that the protons attached to C₂ are more deshielded. The calculated isotropic chemical for these sites is 4.4 ppm, with the following principal components: 13.4, 4.0, and –4.0 ppm. Similar to the protons on C₁, the most shielded component of the protons on C₂ lies normal to the plane of the Au atoms. For the remaining protons on the octyl chain, the most shielded component begins to deviate from the *z* axis. However, the shielding along this axis remains shielded compared to the isotropic value, the ¹H NMR chemical shift normal to the Au plane ranges from 0.1 to –4.4 ppm for the methylene protons. Therefore, ¹H NMR measurements of a monolayer of thiol on a gold surface placed perpendicular to the direction of an applied magnetic field should yield a wide resonance centered at a shielded direc-

tion compared to the resonance of the protons in tetramethylsilane.

4. Conclusions

This work has shown that ¹³C shielding calculations of octanethiols bound to Au are sensitive to the type of Au–S bonding. This sensitivity explains the experimental observation [9,10] that the resonances of the carbons closest to the S headgroup are broad. Furthermore, the results indicate that best agreement with experiment is achieved when the S atom of the thiol is placed on a threefold hollow site. Based on the *ab initio* results, several trends are seen with regard to the tensors, which may become accessible in future experiments.

Acknowledgements

This work was supported in part by a CAREER Award from the National Science Foundation under Grant No. CHE-9874424. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Dr R.E. Gerald II and Prof. C.A. Foss for useful discussions.

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