

Gold–Sulfur Interactions in Alkylthiol Self-Assembled Monolayers Formed on Gold Nanoparticles Studied by Solid-State NMR

A. Badia, L. Demers, L. Dickinson, F. G. Morin, R. B. Lennox,* and L. Reven*

Department of Chemistry, McGill University
801 Sherbrooke Street West
Montreal, Quebec, Canada H3A 2K6

Received July 31, 1997

A definitive description of metal–sulfur bonding in alkylthiol self-assembled monolayers (SAMs) formed on gold surfaces is central to understanding issues related to chain order, thermal stability, and formation kinetics.¹ Suggested bonding modes include gold thiolates (RS[−])¹ and dialkyl disulfides.² The evidence for the existence of either a thiolate or a disulfide is inferential and ambiguous.^{2,3} This fundamental structural issue remains as yet unresolved because many of the surface characterization techniques applied to these monolayers are unable to differentiate surface bonding states. The most commonly used organic structural tool, NMR, cannot however be applied to monolayers on planar substrates for sensitivity reasons. We have therefore sought a high surface area analog to the planar SAMs which is amenable to a detailed NMR structural study. In this regard, we and others have been attracted to the RS/Au nanoparticle system prepared by Schiffrin and co-workers,^{4–9} a direct link between planar and these nanoparticle SAMs has been made as (i) there is an excellent correspondence between the chainlength-dependent order/disorder phase transitions observed in the two systems,^{5,10} (ii) the nanoparticles are highly faceted with (111) and (100) single crystal faces,⁸ and (iii) FT-IR studies report very similar gauche bond population distributions along the alkyl chains.^{5a,c,6b} The RS/Au interactions in these two systems are evidently closely related given that surface bonding controls features such as alkyl chain spacing, chain tilt, and cooperative phenomena which lead to chain order/disorder transitions.^{5,10} XPS data suggests that the RS/Au bonding is the same in these two systems.^{4a,8a,9,11}

* Authors to whom correspondence should be addressed at the following: e-mail bruce_lennox@maclean.mcgill.ca or linda_reven@maclean.mcgill.ca.

- (1) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
- (a) Fenter, P.; Eberhardt, A.; Eisenberger, P. *Science* **1994**, *266*, 1216. (b) Gerdy, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1996**, *118*, 3233. (c) Nishida, N.; Hara, M.; Sasabe, H.; Knoll, W. *Jpn. J. Appl. Phys. Part 1* **1996**, *35*, 5866. (d) Nishida, N.; Hara, M.; Sasabe, H.; Knoll, W. *Jpn. J. Appl. Phys. Part 2* **1996**, *35*, L799. (e) Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528.
- (a) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358. (b) Strong, L.; Whitesides, G. M. *Langmuir* **1988**, *4*, 546. (c) Bain, C. D.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1989**, *5*, 723.
- (a) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 802. (b) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. *Chem. Soc., Chem. Commun.* **1995**, 1655.
- (a) Badia, A.; Singh, S.; Demers, L. M.; Cuccia, L. A.; Brown, G. R.; Lennox, R. B. *Chem. Eur. J.* **1996**, *96*, 2657. (b) Badia, A.; Gao, W.; Singh, S.; Demers, L.; Cuccia, L.; Reven, L. *Langmuir* **1996**, *12*, 1262. (c) Badia, A.; Cuccia, L.; Demers, L.; Morin, F. G.; Lennox, R. B. *J. Am. Chem. Soc.* **1997**, *119*, 2682.
- (a) Terrill, R. H.; et al. *J. Am. Chem. Soc.* **1995**, *117*, 12537. (b) Hostetler, M. J.; Stokes, J. J.; Murray, R. W. *Langmuir* **1996**, *12*, 3604. (c) Hostetler, M. J.; Murray, R. W. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 42.
- Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, *99*, 7036.
- (a) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murphy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428. (b) Luedtke, W. D.; Landman, U. *J. Phys. Chem.* **1996**, *100*, 13323.
- Johnson, S. R.; Evans, S. D.; Mahon, S. W.; Ulman, A. *Langmuir* **1997**, *13*, 51.
- Badia, A.; Back, R.; Lennox, R. B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2332.

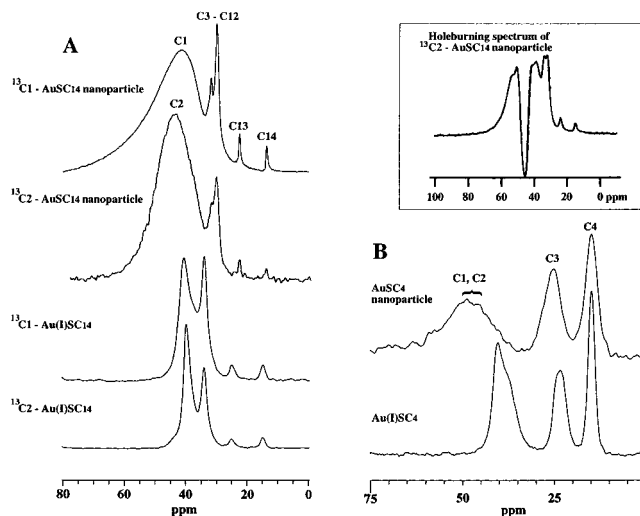


Figure 1. Solid-state (67.92 MHz) CPMAS ¹³C NMR spectra of (A) [1-¹³C]- and [2-¹³C]-labeled CH₃(CH₂)₁₂CH₂S/Au nanoparticles and [Au{SC₁₄H₂₉}]_n complexes. (B) C₄H₉S/Au nanoparticles and the [Au{SC₄H₉}]_n complex. Inset: ¹³C CPMAS spectrum of ¹³C-Au/SC₁₄ colloids with selective irradiation.¹⁹

The solid-state ¹³C NMR spectra of unlabeled short-chain (C₄) and isotopically-labeled long-chain (C₁₄) alkylthiols bound to gold nanoparticles are shown in Figure 1; the chemical shifts are summarized in Table 1. Selective ¹³C labeling of carbons 1 and 2 was necessary to both enhance and resolve these signals which are weak as a result of extensive line broadening.^{5a,b} In the [1-¹³C]- and [2-¹³C] labeled C₁₄S/Au nanoparticles, broad resonances are observed which are shifted *downfield* by 18 ppm for C1 and 12 ppm for C2 compared to the free thiol values. The C1 and C2 shift values allow one to rule out the occurrence of weakly associated organosulfur species which may either be byproducts of the synthesis, such as simple thiolates (RS[−]Na⁺ form)⁴ and alkyl disulfides,¹¹ or air oxidation products, such as alkylsulfonates.¹² A physisorbed thiolate is ruled out since the downfield shifts, from the free thiol, of C1 (1.7 ppm) and C2 (5.2 ppm) of the C₁₄ thiolate salt are much smaller than those observed for the Au/SC₁₄ colloids. Likewise, the ¹³C chemical shift trend of the C1 and C2 methylenes allows us to eliminate the possibility of a weakly bound disulfide or sulfonate. Whereas C2 is *upfield* from C1 by 9.6 ppm in the C₁₄ disulfide and by 22.9 ppm in the sulfonate, C2 is 4 ppm *downfield* from C1 in the Au/CS₁₄ nanoparticles.

Given these NMR data, what is the origin of the striking C1 shift in the thiol-derivatized nanoparticles? We considered that the large C1 shift in these nanoparticles may have a contribution from the conduction electrons of the gold core (Knight shift). For metals such as Pt and Pd, adsorbate Knight shifts are identifiable when (i) the relaxation follows the Korringa law and (ii) the ¹³C shifts are much greater than the normal chemical shift range of diamagnetic organometallic compounds.¹³ In these modified nanoparticles, the C1 spin–lattice relaxation time (T₁) does not exhibit Korringa behavior, which manifests itself as a linear relationship between T₁ and temperature. Instead, the observed T₁ temperature dependence is typical of dipolar relaxation in the slow limit side of the correlation time *vs* T₁ curve.¹⁴ In order to definitively exclude a large metallic

(11) Castner, D. G.; Hinds, K.; Grainger, D. W. *Langmuir* **1996**, *12*, 5083.

(12) (a) Tarlov, M. J.; Newman, J. G.; *Langmuir* **1992**, *8*, 1398. (b) Riely, H.; Price, N. J.; White, R. G.; Blyth, R. I. R.; Robinson, A. W. *Surf. Sci.* **1995**, *331–333*, 189.

(13) Ansermet, J.-Ph.; Slichter, C. P.; Sinfelt, J. H. *Prog. NMR Spectrosc.* **1990**, *22*, 401. Carbon-13 Knight shifts have been observed only for carbons which are *directly* bonded to metals.

Table 1. Carbon-13 Chemical Shifts (δ (ppm)) for R = C₄H₉S and C₁₄H₂₉S

	thiol	thiolate	disulfide	sulfonate	complex	nanoparticles	
C ₄ H ₉	C ₄ H ₉ SH ^a	C ₄ H ₉ SNa ^a	(C ₄ H ₉ S) ₂ ^b		Au(I)SC ₄ H ₉ ^c	Au/SC ₄ H ₉ ^c	
C1	24.1	24.1	38.9		40.1(sh at 38) ^d	~46 ^e	1115 ^f
C2	35.9	38.6	31.4		40.1 ^d	~46 ^e	1115 ^f
C3	21.3	21.6	21.7		23.4	25.2	285 ^f
C4	13.3	13.1	13.7		14.7	15.0	265 ^f
C ₁₄ H ₂₉	C ₁₄ H ₂₉ SH ^a	C ₁₄ H ₂₉ SNa ^a	(C ₁₄ H ₂₉ S) ₂ ^a	C ₁₂ H ₂₅ SO ₃ Na ^a	Au(I)SC ₁₄ H ₂₉ ^c	Au/SC ₁₄ H ^c	
C1	24.5	26.2	39.2	52.74	40.1(sh at 38) ^{g,h}	~42 ^h	1300 ^f
C2	33.9	39.1	29.6	29.87	39.4 ^h	~46 ^h	1015 ^f

^a Solution spectrum. ^b From *Sadtler Handbook of Carbon-13 Spectra*. ^c Solid-state spectrum. ^d Deconvolution yields two peaks integrating at 3:1. ^e Integration yields two carbons. ^f Values are given in $\nu_{1/2}$ (Hz). ^g Two peaks integrate as 1:1. ^h From ¹³C-labeled thiol.

contribution to the C1 shift, the NMR properties of diamagnetic Au(I) alkylthiolates, [Au(I){SC_nH_{2n+1}}]_n, were also studied. The vast majority of Au(I) thiolates have been reported to be 2-coordinate with linear polymeric or ring structures.¹⁵ The C1 and C2 resonances in the [Au(I){SC₁₄H₂₉}]_n and [Au(I){SC₄H₉}]_n complexes are coincident ($\delta \approx 40$ ppm) and shifted *downfield* from the free thiol values by ~ 16 ppm for C1 and ~ 4 – 5 ppm for C2 (Table 1). The striking similarity of the ¹³C shifts between the [Au(I)SR]_n complexes and the Au/SR nanoparticles (Figure 1) allows us to use these molecular complexes as structural analogues and rule out a metallic contribution. Thus, the large downfield chemical shifts observed for C1 and C2 originate from the Au–S interaction.

We therefore ask: what form *does* the Au–S interaction take? The C1 shifts in the Au(I) alkylthiolate complexes (40 ppm) and Au/SC₁₄ particles (42 ppm) are close to that of unbound dialkyl disulfides (39 ppm). This could mean that the organosulfur is in the form of a disulfide in the complex and, by inference, in the colloid. However, very similar ¹³C shifts are observed in (AgSR)_n complexes where the bridging organosulfur is exclusively in the thiolate and not the disulfide form.¹⁶ In addition, Raman spectra of the Au(I) thiolates are not consistent with the presence of a bridging disulfide. The coincidence of the C1 chemical shifts of unbound dialkyl disulfides and Au(I) alkylthiolates is apparently fortuitous. We conclude that a chemisorbed disulfide in the colloid system is very unlikely. These relationships instead support a metal–thiolate bond.

Another noteworthy feature of the carbon NMR spectra is the broadness ($\nu_{1/2} \approx 1000$ – 1300 Hz) of the C1 and C2 resonances of the RS/Au nanoparticles. The C1 and C2 line widths, which vary linearly with field strength, are only partially reduced by magic angle spinning (MAS). The residual linewidth in the solid-state which is not averaged out by MAS must be due to a shift or shift-like distribution.^{17,18} MAS eliminates the chemical shift anisotropy *and* the isotropic bulk magnetic

susceptibility (BMS) broadening. However, a *distribution* of isotropic shifts will not be averaged by MAS. A hole burning experiment¹⁹ of the [¹³C₂]-C₁₄S/Au nanoparticles with MAS (Figure 1, inset) confirms that these resonances are heterogeneously broadened. Broadening of the C1 and C2 resonances most probably arises from a distribution of shifts due to different chemisorption sites and/or nonspherical particle shapes. The highly faceted morphology of the thiol-derivatized gold nanoparticles would give rise to an inhomogeneously broadened line since thiolates adsorbed on either of the face types of the small crystallites will exhibit different average chemical or BMS shift values compared to thiolates adsorbed in less symmetrical sites at edges and corners. The linewidth values for the short-chain and ¹³C-labeled long-chain thiols (Table 1) reveal that the broadening interaction drops off sharply along the alkyl chain. Since the BMS effect drops off more gradually along the chain, a chemical shift distribution is probably the major contributor to the line broadening.¹⁸

In summary, the chemisorbed species on the gold nanoparticle surface is most probably a thiolate, not a disulfide, given the similarity in the ¹³C chemical shifts of the Au/SR colloids and Au(I) alkylthiolates. The interactions responsible for the line broadening of the C1 and C2 sites are consistent with the particles being faceted. No evidence for a Knight shift contribution to the C1 shift is observed. The excellent correspondence observed thus far, between the properties of thiols adsorbed on planar and colloid surfaces, indicates that conclusions based on ¹³C NMR studies of gold–sulfur interactions in the nanoparticle system are transferable to the planar RS/Au SAMs.

Acknowledgment. We thank NSERC (Canada) and FCAR (Quebec) for financial support. This research was funded in part by a Grant-in-Aid of Research to A.B. from Sigma Xi (USA).

Supporting Information Available: Synthetic procedures and Raman data (2 pages). See any current masthead page for ordering and Internet access instructions.

JA9726163

(14) A small conduction electron contribution to the shift could be definitively eliminated only with a perdeuterated sample because a small Korringa contribution would be masked by the dipolar relaxation. The NMR relaxation measurements and line shape calculations will be presented in a later publication.

(15) (a) Brown, K.; Parish, R. V.; McAuliffe, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 4943. (b) Al-Sa'ady, A. K. H.; Moss, K.; McAuliffe, C. A.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1984**, 1609.

(16) Fijolek, H. G.; Grohal, J. R.; Sample, J. L.; Natan, M. J. *Inorg. Chem.* **1997**, *36*, 622.

(17) Zilm, K. W.; Bonneviot, L.; Hamilton, D. M.; Webb, G. G.; Haller, G. L. *J. Phys. Chem.* **1990**, *94*, 1472.

(18) As noted in ref 17, a small concentration of paramagnetic species could also contribute to the line broadening. EPR studies of the gold nanoparticles are in progress.

(19) Caravatti, P.; Bodenhausen, G.; Ernst, R. R. *J. Magn. Reson.* **1983**, *55*, 88.