J. Am. Chem. Soc. **2001,** *123,* 769−770

Effect of Laser Fluence on Laser Desorption Mass Spectra of Organothiol Self-Assembled Monolayers on Gold

Weihong Gong, Vassil I. Elitzin, Selvasekaran Janardhanam,
Charles L. Wilkins,* and Ingrid Fritsch*

Department of Chemistry and Biochemistry
University of Arkansas, Fayetteville, Arkansas 72701

Received September 3, 2000

Organothiol self-assembled monolayers (SAMs) on gold are promising candidates for a wide range of applications, such as electron transport studies, biosensors, models for biomembranes, and microelectronic devices. They are especially attractive because of the strength of the Au−S bond. There is extensive literature documenting the relative ease of preparing such SAMs.[1] A great many techniques have been applied to the characterization of SAMs, but in recent years, mass spectrometric methods have been increasingly used. Laser desorption mass spectrometry (LDMS) possesses the requisite sensitivity and specificity required for studying the chemistry of self-assembled monolayers. However, when different lasers are used to study the same types of SAMs, the spectral results are not always consistent. As is shown here, laser fluence, rather than laser wavelength, as previously suggested,[2] is a major determinant of the spectral observations.

To put the present work in context, it is useful to consider recent reports of negative ion LDMS of thiol SAMs by Trevor, et al.[2,3] In their study, when a 212 nm laser was used for direct LDMS, to obtain negative ion spectra of alkanethiolate SAMs on gold, only RS^-, RSO_2^-, and RSO_3^-, anions were observed, and no dimer ions were seen, consistent with the previous published Fourier transform mass spectometry studies.[4,5] Trevor, et al. explained these results by proposing that ionization in negative ion LDMS of SAMs occurrred by electron attachment to desorbed neutrals. SAMs investigated by negative ion 337 nm LDMS gave only small fragment ions and neither monomer nor dimer ions.[2] Thus, the presence of negative ions from monomers and oxidation products in the 212 nm LDMS as well as the 193 and 308 nm literature spectra[4,5] was attributed to electron photoemission at energies of ≥4.0 eV. However, the 3.7 eV energy of 337 nm photons was said to be insufficient to serve as a source of electron attachment to ionize desorbed neutrals. The present results clearly eliminate single-photon electron photoemission as a factor in the LDMS of the SAMs studied.

Our own recent negative ion LDMS studies of several alkanethiolate SAMs[6] give spectra containing abundant ions with composition corresponding to gold adducts of dimers, not reported by Trevor, et al.[2] In an effort to understand these observations, we have investigated the effects of laser fluence and pulsed-ion extraction (PIE) delay time upon the spectra obtained. An instrument equipped with two lasers, a Nd:YAG laser operated at either 266 or 532 nm and a N_2 laser operated at 337 nm, was used to obtain negative ion mass spectra for the same samples.[7] Sample-to-sample variation was minimized by optics which permitted use of both lasers on each sample, without removing or repositioning the sample. Because the samples are prepared and placed in the spectrometer with rigorous exclusion of air and ozone, no peaks corresponding to oxidation products are seen in any of the present spectra. As is now established, ozone easily oxidizes alkanethiol SAMs,[8−10] and its presence in air could certainly explain earlier observations of air oxidation.[4,5] Interestingly, when the 337 nm nitrogen laser is used, only a peak with a mass corresponding to a $[Au(RS)_2]^-$ species is seen. However, the Nd:YAG laser desorption spectrum has both RS^- and $[Au(RS)_2]^-$ peaks. Observations of $[Au(RS)_2]^-$ adduct ions are not unprecedented and have previously been reported for TOF secondary ion mass spectrometry (SIMS) of both homogeneous and mixed thiol SAMs (with mixed adduct anions observed in the latter case).[11,12] Gold anions are not observed in most spectra because fluence was generally adjusted to be below the threshold for gold desorption.

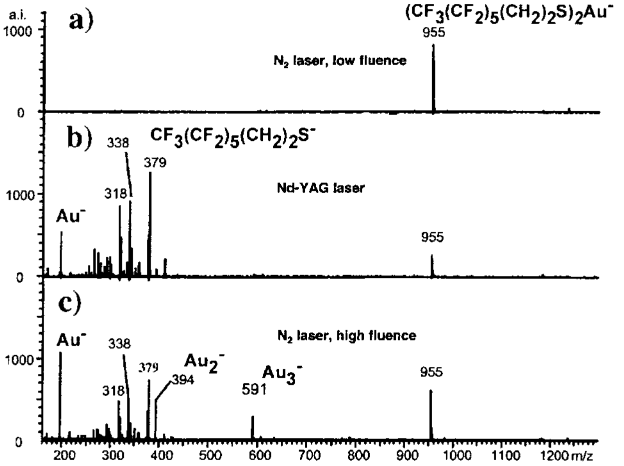

Figure 1. Comparison of nitrogen laser desorption and Nd:YAG laser desorption TOF spectra of the 1,1,2,2-tetrahydroperfluorooctanethiol SAM at various fluences: (a) 0.3×10^8 W/cm^2; (b) 0.5×10^8 W/cm^2; (c) 0.4×10^8 W/cm^2.

One possible interpretation of our results would be that the difference between energy of photons from the 337 nm nitrogen laser and that of the photons from the 266 nm Nd:YAG laser is responsible for the differences in mass spectra resulting from using these two lasers with the same samples. To explore this premise, the Nd:YAG laser output was attenuated to reduce the fluence. Under these circumstances, the direct LDMS negative ion spectra obtained from either decanethiol or dodecanthiol SAMs using the Nd:YAG laser showed only $[Au(RS)_2]^-$ ions. Furthermore, when the partially fluorinated thiol $[CF_3(CF_2)_5(CH_2)_2SH]$[13] SAM was subjected to LDMS by the N_2 laser at a low (0.3×10^8 W/cm^2)

---

(1) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533−1554.

(2) Trevor, J. L.; Hanley, L.; Lykke, K. R. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 587−589.

(3) Trevor, J. L.; Lykke, K. R.; Pellin, M. J.; Hanley, L. *Langmuir* **1998**, *14*, 1664−1673.

(4) Li, Y.; Huang, J.; R. T. McIver, J.; Hemminger, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2428−2432.

(5) Scott, J. R.; Baker, L. S.; Everett, W. R.; Wilkins, C. L.; Fritsch, I. *Anal. Chem.* **1997**, *69*, 2636−2639.

(6) Self-assembled monolayers of 1-decanethiol, 1-dodecanethiol, and 1,1,2,2-tetrahydroperfluorooctanethiol were prepared by immersion of clean substrates in 1 mM ethanol solutions of the thiols for 24 h. The substrates consisted of glass coated with a 50 Å chromium adhesion layer and a top layer of 2000 Å of gold. (See ref 5 for details of the cleaning procedure.) Self-assembled monolayers of 11-ferrocenylundecanethiol were prepared similarly by using a 0.1 mM ethanol solution of the thiol. All samples were kept in argon atmospheres, prior to mass spectral analysis.

(7) Mass spectra were measured with a Bruker Reflex III (Bruker Daltonics) reflectron time-of-flight mass spectrometer equipped with a nitrogen laser (337 nm, Laser Science, Inc.) and a Nd:YAG laser (266 or 532 nm New Wave Research, Inc.). Spectra were obtained in reflectron negative ion mode at a background pressure of 10^{-8} mbar. Each spectrum resulted from adding 10 spectra, each obtained at a different spot on the sample.

(8) Norrod, K. L.; Rowlen, K. L. *J. Am. Chem. Soc.* **1998**, *120*, 2656−2657.

(9) Schoenfisch, M. H.; Pemberton, J. E. *J. Am. Chem. Soc.* **1998**, *120*, 4502−4513.

(10) Zhang, Y. M.; Terrill, R. H.; Tanzer, T. A.; Bohn, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 2654−2655.

(11) Offord, D. A.; John, C. M.; Griffin, J. H. *Langmuir* **1994**, *10*, 761−766.

(12) Tarlov, M. J.; Newman, J. G. *Langmuir* **1992**, *8*, 1398−1405.

(13) Chidsey, C. D. E.; Loicono, D. N.; *Langmuir* **1990**, *6*, 682−691.

10.1021/ja0055716 CCC: $20.00

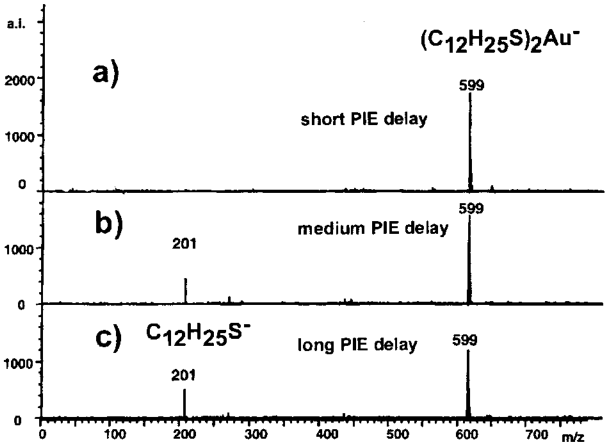

Figure 2. Comparison Nd:YAG laser desorption spectra of dodecanethiol SAMs at: (a) 250 ns PIE delay; (b) 400 ns PIE delay; (c) 700 ns PIE delay. Average fluence 0.6 × 10^8 W/cm^2.

fluence, only $[Au(RS)_2]^-$ ions were observed (Figure 1a). When a higher (0.4 × 10^8 W/cm^2) fluence was used, *both* monomer RS^- and $[Au(RS)_2]^-$ anions (ratio $RS^-/[Au(RS)_2]^- = 1.2$) in addition to Au^-, Au_2^-, and Au_3^- ions were observed (Figure 1c). The resemblance of the latter spectrum to the Nd:YAG laser desorption spectrum in Figure 1b (fluence 0.5 × 10^8 W/cm^2) is obvious. Further, when the Nd:YAG laser was adjusted to produce 532 nm output and LDMS negative ion spectra of decanethiol and dodecanethiol SAMs obtained for different fluences similar spectral behavior was found. Lower fluence LDMS produced only $[Au(RS)_2]^-$ ions, and higher fluence LDMS resulted in *both* monomer RS^- and $[Au(RS)_2]^-$ anions. Ratios of $RS^-/[Au(RS)_2]^-$ are 2.2 for decanethiol and 1.3 for dodecanethiol SAMs. These facts are consistent with the hypothesis that laser fluence, not wavelength, determines the appearance of the resulting spectrum. Wavelength dependence, if any, is minimal.

Finally, when the PIE delay was varied, to retain ions in the source for various times following desorption with the Nd:YAG laser at 266 nm (250, 400, or 700 ns), prior to spectral acquisition, results such as those in Figure 2 were obtained. Clearly, the relative ratio of RS^- to $[Au(RS)_2]^-$ increased for the alkanethiolate SAMs. Accordingly, we conclude that a controlling factor in the spectral differences seen in LD-TOF mass spectra is a kinetic effect, reflecting differences in source residence time and laser fluence, not relative photon energy. A plausible model is that initial desorption leads to formation of $[Au(RS)_2]^-$. Subsequently, if the laser fluence is sufficient, these adducts dissociate into the monomer species. The degree to which this dissociation occurs is also a function of the adducts' residence time in the source region, with longer times permitting more dissociation to monomer at any particular fluence chosen.

Acknowledgment. Support from the National Science Foundation through Grants CHE-92-01277(C.L.W.), CHE-99-82045 (C.L.W.), and CHE-96-24114 (I.F.) is gratefully acknowledged.

Supporting Information Available: Eight figures with typical LD-TOF mass spectra of all four types of self-assembled monolayers studied, using both N_2 (337 nm) and Nd:YAG (266 and 532 nm) lasers at various fluences and PIE delays. Fluence ranges reported are the highest and lowest values determined for 10 measurements of fluence for each sample. Tables giving $RS^-/[Au(RS)_2]^-$ ratios and summarizing fluences for all measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0055716