

A Raman Spectroscopy Study of SO_x Species Adsorbed on Au Nanocluster Surfaces

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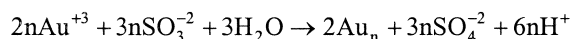
ABSTRACT

Raman spectroscopy is employed to study the reaction of Au³⁺ with SO₃⁻². The Raman spectra of Au³⁺/SO₃⁻² reaction mixtures are characterized by Raman peaks between 1000 and 1200 cm⁻¹. These Raman peaks are drastically different from bands observed in the Raman spectra of SO₃⁻² or SO₄⁻², the product of SO₃⁻² oxidation. These bands are attributed to the formation of SO_x species on gold nanocluster surfaces. Theoretical calculations at the MP2 level are consistent with the experimental observations and predict an increase in frequencies of S-O deformation modes upon adsorption on gold cluster surfaces.

Keywords: gold nanoclusters, nanoparticles, adsorption, nanocluster surface, Raman, MP2 calculations, colloids.

INTRODUCTION

Chemical environment plays a major role in optical and electronic properties of gold nanoclusters [1,2]. A number of chemical species are proposed to adsorb on gold nanocluster surfaces [3,4]. Adsorbed species can have different effects on the properties of gold nanoclusters and little is known about reactions on the surface of these clusters [5,6,7]. Several methods are employed for gold nanoparticle synthesis. The synthesis of gold colloids is among the most used. Recent work by Murrillo and coworkers has established that the reaction of sulfite, SO₃⁻², with Au³⁺, leads to the synthesis of gold colloids according to the following general reaction [8,9]:



reaction 1

Au³⁺ is reduced by SO₃⁻² in time scales of the order of a few milliseconds [9]. The synthesis of clusters with sizes up to about 200 nm is deduced from model fits to optical absorption data with Mie scattering theory [8,9]. We have used reaction 1 as a model for the development of methods to study surface processes that occur in gold colloid synthesis. We report here in situ Raman measurements in gold nanocluster synthesis based on reaction 1.

RAMAN MEASUREMENTS

Results from our Raman measurements are summarized on tables 1 and 2. Raman measurements on the SO₃⁻² solution employed for the experiments reported here revealed a strong band centered at 962 cm⁻¹ due to S-O stretching. Experiments were also performed on SO₄⁻², the product of SO₃⁻² oxidation. The Raman spectrum of a SO₄⁻² containing salt revealed a strong band at 987 cm⁻¹ and peaks of smaller intensities centered at about 1098 and 1138 cm⁻¹. Comparison with previous works facilitates the assignment of the bands observed in the Raman spectrum of SO₄⁻².¹² The strong Raman peak at 987 cm⁻¹ is assigned to the symmetric S-O stretch in the SO₄⁻² anion. The vibrational frequency of this mode appears at 968 cm⁻¹ in aqueous solutions saturated in SO₄⁻². The weak intensity peaks at 1098 and 1138 cm⁻¹ are not observed in the Raman spectrum of aqueous solutions saturated in SO₄⁻².

SO ₃ ⁻²	962
SO ₄ ⁻² (salt)	987
SO ₄ ⁻² solution	976

Table 1: Raman shifts (cm⁻¹) of the S-O stretch for SO₃⁻², SO₄⁻² (salt) and SO₄⁻² (solution). See text for details.

Table 2 summarizes the bands found in the Raman spectra of Au^{3+} and SO_3^{-2} reaction mixtures. The $[\text{SO}_3^{-2}]/[\text{Au}^{3+}]$ concentration ratios where the different species appear are also indicated on table 1. No evidence for SO_x species were found in the Raman spectra between 850 and 1250 cm^{-1} until a $[\text{SO}_3^{-2}]/[\text{Au}^{3+}]$ concentration ratio of 6 was reached. Raman signals at 976, 1010, 1046, 1121 and 1146 cm^{-1} are observed in the Raman spectrum for $[\text{SO}_3^{-2}]/[\text{Au}^{3+}]$ concentration ratios between 6 and 10. The band at 976 cm^{-1} is assigned to the symmetric S-O stretch in SO_3^{-2} by comparison with the spectrum of aqueous solutions saturated in SO_4^{-2} . The bands at 1010, 1046, 1121 and 1146 cm^{-1} are attributed to chemical species different from SO_3^{-2} or SO_4^{-2} , as they are not observed in the Raman spectra of these two sulfur oxides.

$[\text{SO}_3^{-2}]/[\text{Au}^{3+}]$ concentration ratio	Raman shift (cm^{-1})	assignment
0 to 4	none	none
6 to 10	976; 1010, 1046,1121,1146	SO stretch in SO_4^{-2} ; $\text{SO}_x\text{-Au}_n$
12 to 30	976; 968; 1010 and 1046	SO stretch in SO_4^{-2} ; SO stretch in SO_4^{-2} ; $\text{SO}_x\text{-Au}_n$

Table 2: Raman shifts (in cm^{-1}) between 850 and 1250 cm^{-1} for different $[\text{SO}_3^{-2}]/[\text{Au}^{3+}]$ concentration ratios. Tentative assignments of these bands are indicated on the table. See text for details.

The Raman peaks at 1121 and 1146 cm^{-1} completely disappear when a $[\text{SO}_3^{-2}]/[\text{Au}^{3+}]$ concentration ratio of 12 was reached. For this $[\text{SO}_3^{-2}]/[\text{Au}^{3+}]$ concentration ratio, a band at 968 cm^{-1} develops: this band is attributed to the accumulation of excess SO_3^{-2} in the reaction mixture. The bands at 1010 and 1046 cm^{-1} were observed for $[\text{SO}_3^{-2}]/[\text{Au}^{3+}]$ concentration ratios as high as 30, the highest ratio employed in the present study.

It is now well established that SO_3^{-2} reduces Au^{3+} to Au^0 , which undergoes a number of coupling reactions to form gold nanoclusters [8,9]. Evidence of gold nanocluster formation on the Au^{3+} and SO_3^{-2} reaction mixtures described above was found in UV-visible measurements. The plasmon resonance peak attributed to gold nanoclusters was observed between 500 and 600 nm. The Raman peaks at 1021, 1046, 1121 and 1146 cm^{-1} are attributed to the formation of SO_x species on gold nanocluster surfaces.

THEORETICAL CALCULATIONS

Theoretical calculations at the MP2 level were performed with the purpose of learning about the $\text{SO}_x\text{-Au}_n$ species that lead to the appearance of the Raman peaks between 1000 and 1200 cm^{-1} . The chemical species considered included SO_4^{-2} , AuSO_4 , SO_3^{-2} and AuSO_3 . Results are summarized on table I. The calculations predict S-O deformation modes at 708 cm^{-1} . The highest frequency band observed in the Raman measurements on SO_3^{-2} is centered at 968 cm^{-1} . Assuming the calculated frequency at 708 cm^{-1} corresponds to the same mode as the one observed at 968 cm^{-1} , we estimate a scaling factor of 1.367. This value was used as a first approximation to scale calculated SO_3^{-2} vibrational frequencies summarized in table 3. Using this value, the calculations predict high frequency bands at 1149 and 1060 cm^{-1} for AuSO_3 .

Calculations were extended to SO_4^{-2} and AuSO_4 . The calculations revealed a mode at 728 cm^{-1} that was taken as the one corresponding to the band measured at 976 cm^{-1} ; a scaling factor of 1.34 was deduced from this assignment. A number of scaled frequencies between 1000 and 1250 cm^{-1} are predicted for AuSO_4 . The calculations were extended to Au_2SO_4 and Au_3SO_4 . The general trend observed was a slight increase the number and values of frequencies above 1000 cm^{-1} .

Species	Calculated shift (cm^{-1})	Raman
SO_3^{-2}	968 (708)	
AuSO_3	1149 (841) 1060 (776)	
SO_4^{-2}	976 (728) 1190 (888)	
AuSO_4	1244 (928) 1238 (924) 1067 (797) 900 (672)	

Table 3: Predicted Raman shifts between 1000 and 1250 cm^{-1} for SO_3^{-2} , AuSO_3 , SO_4^{-2} and AuSO_4 obtained at the MP2 level. Non scaled frequencies are in parenthesis. See text for details

DISCUSSION

The Raman measurements are consistent with an increase in the S-O stretching frequency upon adsorption of SO_x species on gold nanocluster surfaces. The theoretical

calculations are consistent with this interpretation. Calculated Raman shifts corresponding to deformation modes that appear in the S-O stretch region of the spectrum increase upon formation of AuSO₄ or AuSO₃. This result supports the assignment of the bands between 1000 and 1250 cm⁻¹ in the Raman spectra of reaction mixtures of Au³⁺ and SO₄⁻² to the formation of adsorbed SO_x species on gold clusters, i.e., Au_nSO₄ and/or Au_nSO₃ species (n ≥ 1). The oxygen atoms screen the sulfur atom in SO₄⁻². Thus, any adsorption of SO₄⁻² on the nanocluster surface must occur by the oxygen atoms. The molecular geometry of SO₃⁻², on the other hand, could allow for interactions between the sulfur and gold atom. The formation of AuSO_x species has been reported in the context of oxidation and degradation of alkyl thiol monolayers.¹¹ The results presented here represent the first evidence on the adsorption of SO_x on nanocluster surfaces.

The size of the gold nanocluster or the sulfur to oxygen ratio of the species adsorbed on the nanocluster surface is still an open question. Further work with near field optical techniques is required to fully characterize the species formed on the surface of gold nanocluster during the synthesis process.

REFERENCES

1. L. Clarke, M N Wybourne, L O Brown, J E Hutchison, M Yan, S X Cai and J F W Keana, *Semicond. Sci. Technol.* **13**, A111-A114, (August 1998) .
2. P. Galletto, P. F. Brevet, and H. H. Girault and R. Antoine and M. Broyer, *J. Phys. Chem. B*, **103** (41), 8706-8710, (1999).
3. Schmid, G., *J. Chem. Soc., Dalton Trans*, **1077**, 1998.
4. Robert E. Benfield and Didier Grandjean *J. Phys. Chem. B*, **105** (10) , 1961 -1970, (2001).
5. Ivan R. Videnovic, Verana Thommen, Peter Oelhafen, Daniel Mathys, Marcel Duggelin and Richard Guggenheim, *Applied Physics Letters*, Vol. **80**(16), 2863–2865, (April 2002).
6. M. Haruta, *Catal. Today* **36**, 153, (1997).
7. T. Akita, K. Tanaka, S. Tsubota, and M. Haruta, *J. Electron Microsc.* **49**, 657 (2000).
8. Growth kinetics of gold nanoparticles"; L.E. Murrillo, O. Viera, Julio G. Briano, Miguel E. Castro, Y. Ishikawa, R. Irizarry, L. Solá,, *Proceedings of the International Conference on Computational Nanoscience and Nanotechnology, (ICCN 2002)*, Chapter 16, Materials and Nanostructures Studies, pages 435-438. web address <http://www.comppub.com/publ/ICCN2002/W62.13.pdf>
9. Luis E. Murrillo, M.S. Thesis, The University of Puerto Rico at Mayaguez, May (2001).
10. Miguel E. Castro, Bertina Posada, Liza Mercado, Julio Briano, Roberto Irizarry and Luis Sola, in preparation.
11. Jessica Torres, Christopher C. Perry, Stephen J. Bransfield and D. Howard Fairbrother, *J. Phys. Chem. B*, **106**, p.6265-6272, (2002).
12. Daimay Lin-Vien, Narman B. Colhup, William G. Fateley and Jeanette G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, (1991).