J|A|C|S
ARTICLES
Published on Web 08/08/2006

# Chiral *N*-Isobutyryl-cysteine Protected Gold Nanoparticles: Preparation, Size Selection, and Optical Activity in the UV−vis and Infrared

Cyrille Gautier and Thomas Bürgi*

*Contribution from the Université de Neuchâtel, Institut de Microtechnique, Rue Emile-Argand 11, 2009- Neuchâtel, Switzerland*

Received January 5, 2006; E-mail: thomas.burgi@unine.ch

***Abstract:*** We have prepared gold nanoparticles covered with *N*-isobutyryl-L-cysteine and *N*-isobutyryl-D-cysteine, respectively. These particles with a mean particle size smaller than 2 nm are highly soluble in water and are amenable to chiroptical techniques such as vibrational circular dichroism (VCD) and circular dichroism (CD) spectroscopy. Density functional theory shows that the VCD spectra are sensitive toward the conformation of the adsorbed thiol. Based on the comparison between the experimental VCD spectrum and the calculated VCD spectra for different conformers, a preferential conformation of the thiol adsorbed on the gold particles can be proposed. In this conformation the carboxylate group interacts with the gold particle in addition to the sulfur. The particles could furthermore be separated according to their charge and size into well-defined compounds. The optical absorption spectra revealed a well-quantized electronic structure and a systematic red-shift of the absorption onset with increasing gold core size, which was manifested in a color change with particle size. Some compounds showed basically identical absorption spectra as analogous gold particles protected with L-glutathione. This shows that these particles have identical core sizes (10−12, 15 and 18 gold atoms, respectively) and indicates that the number and arrangement of the adsorbed thiol are the same, independent of the two thiols, which have largely different sizes. Some separated compounds show strong optical activity with opposite sign when covered with the D- and L-enantiomer, respectively, of *N*-isobutyryl-cysteine. The origin of the optical activity in the metal-based transitions is discussed. The observations are consistent with a mechanism based on a chiral footprint on the metal core imparted by the adsorbed thiol.

## Introduction

Chemists tend to associate chirality with organic molecules, inorganic salts, and biological materials but not necessarily with metals. The crystal structures of metals are highly symmetric and not chiral. Metal surfaces on the other hand can be chiral and are considered for example as heterogeneous enantioselective catalysts.[1,2] Some high Miller index surfaces of metals such as for example Ag(643) are intrinsically or naturally chiral.[3] Such surfaces have been demonstrated to interact differently with the enantiomers of a chiral compound.[3−7] Another type of chirality is obtained through adsorption and long-range ordering of molecules on nonchiral metal surfaces,[8,9] if the pattern formed by the adsorbate destroys the symmetry of the underlying metal surface. The adsorbate itself does not have to be chiral in this case resulting in a racemic mixture of domains on the surface with opposite chirality.[10] Finally, the adsorption of a chiral molecule[11−14] creates a locally chiral environment near the metal surface. This may lead to a "chiral footprint" on the nonchiral surface,[15] i.e., the slight distortion of the metal surface atoms involved in the adsorbate complex toward a chiral arrangement. Adsorbed molecules may also transfer chirality onto the electronic structure of the nonchiral metal.[16]

Monolayer protected metal nanoparticles (MPNs) or clusters are of considerable interest due to their potential application for biosensing,[17] catalysis,[18] electronics,[19] and nanotechnology.[20] These organic−inorganic composite materials have a very large metal surface-to-volume ratio, and in principle the same types

(1) Studer, M.; Blaser, H. U.; Exner, C. *Adv. Synth. Catal.* **2003**, *345*, 45−65.
(2) Bürgi, T.; Baiker, A. *Acc. Chem. Res.* **2004**, *37*, 909−917.
(3) McFadden, C. F.; Cremer, P. S.; Gellman, A. J. *Langmuir* **1996**, *12*, 2483−2487.
(4) Sholl, D. S. *Langmuir* **1998**, *14*, 862−867.
(5) Horvath, J. D.; Gellman, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 2384−2392.
(6) Horvath, J. D.; Koritnik, A.; Kamakoti, P.; Sholl, D. S.; Gellman, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 14988−14994.
(7) Attard, G. A. *J. Phys. Chem. B* **2001**, *105*, 3158−3167.
(8) Lorenzo, M. O.; Baddeley, C. J.; Muryn, C.; Raval, R. *Nature* **2000**, *404*, 376−379.
(9) Lorenzo, M. O.; Haq, S.; Bertrams, T.; Murray, P.; Raval, R.; Baddeley, C. J. *J. Phys. Chem. B* **1999**, *103*, 10661−10669.
(10) Humblot, V.; Raval, R. *Appl. Surf. Sci.* **2005**, *241*, 150−156.
(11) Ferri, D.; Bürgi, T.; Baiker, A. *J. Chem. Soc., Chem. Commun.* **2001**, 1172−1173.
(12) Ferri, D.; Bürgi, T. *J. Am. Chem. Soc.* **2001**, *123*, 12074−12084.
(13) Bieri, M.; Bürgi, T. *J. Phys. Chem. B* **2005**, *109*, 10243−10250.
(14) Bieri, M.; Bürgi, T. *Chem. Phys. Chem.* **2006**, *7*, 514−523.
(15) Humblot, V.; Haq, S.; Muryn, C.; Hofer, W. A.; Raval, R. *J. Am. Chem. Soc.* **2002**, *124*, 503−510.
(16) Hofer, W. A.; Humblot, V.; Raval, R. *Surf. Sci.* **2004**, *554*, 141−149.
(17) Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Science* **1997**, *277*, 1078−1081.
(18) Ghosh, S. K.; Kundu, S.; Mandal, M.; Pal, T. *Langmuir* **2002**, *18*, 8756−8760.
(19) Sun, S. H.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989−1992.
(20) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293−346.

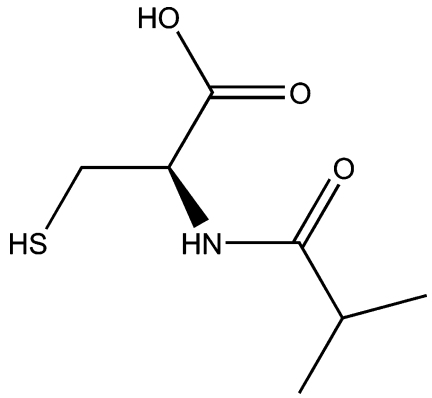
10.1021/ja058717f CCC: $33.50 © xxxx American Chemical Society

of chirality as discussed above for extended metal surfaces could arise. Due to their solubility such particles are amenable to chiroptical techniques such as circular dichroism (CD)[21,22] and vibrational circular dichroism (VCD) spectroscopy,[23−26] which selectively probe their chiral properties. The former technique probes electronic transitions, which may be located in the metal core, whereas the latter is sensitive toward molecular vibrations. We have recently reported for the first time VCD spectra of a chiral thiol, *N*-acetyl-L-cysteine, adsorbed on gold nanoparticles.[27] The study indicated that VCD can be used to obtain structural information on chiral molecules adsorbed on small metal nanoparticles.

Schaaff and Whetten reported optical activity in gold nanoparticles protected with L-glutathione (*γ-glu-cys-gly*).[28] These particles, after preparation, were separated according to their size and charge into well-defined compounds in a gel electrophoresis. The separated compounds, corresponding to particles with a core mass between 4 and 14 kDa (20−70 gold atoms), showed strong optical activity in metal-based transitions. More recently Yao and co-workers reported optical activity in the visible and UV spectral range for gold nanoparticles of 0.6−1.8 nm diameter protected with penicillamine.[29] Three fractions of particles (containing about 6, 50, and 150 gold atoms, respectively) could be separated in a gel electrophoresis. These particles were optically active in the visible and UV spectral range, with the anisotropy factors decreasing with cluster size. In contrast, for the L-glutathione case the smallest particle did not show the highest anisotropy factors.[28] The origin of the observed optical activity and in particular the possibility that the metal core is intrinsically chiral were discussed, but these questions remain open.[28,29] Optical activity was also observed after coating large (23.5 nm) Ag colloids with cysteine, L-glutathione, and penicillamine.[30] It was noted that no optical activity was observed when using gold colloids instead of silver and when using lysine, glutamine, and cysteine methylester as ligands. Based on these observations it was concluded that association of nanoparticles mediated by hydrogen bonding between the adsorbed molecules is responsible for the optical activity. The origin of optical activity in metal-based electronic transitions is still unclear due to the very few examples of well-defined chiral particles described until today and the lack of structural information.

Here we report the preparation, the separation by gel electrophoresis, and chiroptical properties in the UV−vis and infrared of *N*-isobutyryl-L-cysteine (Chart 1) and *N*-isobutyryl-D-cysteine protected gold particles. The vibrational circular dichroism spectra give direct information on the structure of the *N*-isobutyryl-cysteine molecules adsorbed on the metal particles. Up to eight different compounds could be separated in a gel electrophoresis. Some of the separated compounds showed UV−vis spectra very similar to those reported for L-glutathione-protected gold particles. Some separated compounds furthermore exhibited strong optical activity in metal-based transitions, the origin of which is discussed.

***Chart 1.*** Structure of *N*-Isobutyryl-L-cysteine




## Experimental Section

**Materials.** $D_2O$ (99.9%) was received from Cambridge Isotope Laboratories. Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.99%), *N*-isobutyryl-L-cysteine (NILC, 99.5%), *N*-isobutyryl-D-cysteine (NIDC, 99.5%), sodium borohydride ($NaBH_4$, 98%), acrylamide (>99%), *N*,*N*′-methylenebisacrylamide (Bis, >99%), ammonium persulfate (APS, 98%), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, >99.5), and tetraoctylammonium bromide (TOAB, >98%) were purchased from Aldrich, and concentrated (10×) premixed tris(hydroxymethylaminomethane) (Tris)/glycine buffer (250 mM Tris, 1920 mM glycine), 0.5 M Tris-HCl buffer pH 6.8, and 1.5M Tris-HCl buffer pH 8.8 were purchased from BIO-RAD. Water was purified with a Milli-Q system (≥18 MΩ cm). All other chemicals were analysis grade and used as received.

**Synthesis of *N*-Isobutyryl-cysteine Monolayer Protected Nanoparticles (MPNs).** *N*-Isobutyryl-L-cysteine and *N*-Isobutyryl-D-cysteine MPNs were both prepared following a previous report.[27] Briefly, 400 mg of tetrachloroauric acid (1.0 mmol) and 777 mg of the corresponding enantiomer of *N*-isobutyryl-cysteine (4.0 mmol) were dissolved in 200 mL of a methanol/acetic acid solution 6:1 (v/v). The solution rapidly turned red before yielding a cloudy white suspension. This indicates the formation of a Au(I)-*N*-isobutyryl-cysteine polymer. After 30 min, the polymer was reduced by slow addition of a freshly prepared aqueous $NaBH_4$ solution (70 mL, 2.13 mol $L^{-1}$) under vigorous stirring. The mixture was allowed to react for 90 min. The resulting dark solution was filtered using a 0.2 μm PTFE membrane to remove insoluble material and subsequently evaporated under a vacuum at a temperature inferior to 40 °C to near dryness. The nanoparticles were precipitated several times with a large excess of ethanol and filtered using the same 0.2 μm PTFE membrane. The removal of remaining unreacted thiols or disulfides was finally completed by dialysis (Spectra/Por CE) in a bag with a molecular weight cutoff of 3500 Da. Particles were dissolved in 30 mL of water and loaded into the membrane which was then placed in a 2 L beaker of water and slowly stirred. The water was changed every 10 h over the course of 96 h. The black solution was evaporated under a vacuum to yield 340 mg of a black powder.

**Separation of MPNs by Polyacrylamide Gel Electrophoresis (PAGE).** PAGE was performed with a Biorad Protean II XI system with a gel of 3 mm thickness. The experimental conditions for PAGE are close to those employed in previous works.[28] The total contents of the acrylamide monomers were 3% (acrylamide/Bis, 94:6) and 25% (acrylamide/Bis, 93:7) for the stacking gel and separation gel, respectively. The stacking and the separating gels were buffered at pH = 6.8 and 8.8, respectively, with Tris-HCl solution. The eluting buffer

(21) Schellman, J. A. *Chem. Rev.* **1975**, *75*, 323−331.
(22) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671−1682.
(23) Nafie, L. A.; Keiderling, T. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 2715−2723.
(24) Stephens, P. J.; Lowe, M. A. *Annu. Rev. Phys. Chem.* **1985**, *36*, 213−241.
(25) Nafie, L. A. *Annu. Rev. Phys. Chem.* **1997**, *48*, 357−386.
(26) Polavarapu, P. L.; Nafie, L. A. *J. Chem. Phys.* **1980**, *73*, 1567−1575.
(27) Gautier, C.; Bürgi, T. *J. Chem. Soc., Chem. Commun.* **2005**, 5393−5395.
(28) Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2000**, *104*, 2630−2641.
(29) Yao, H.; Miki, K.; Nishida, N.; Sasaki, A.; Kimura, K. *J. Am. Chem. Soc.* **2005**, *127*, 15536−15543.
(30) Li, T.; Park, H. G.; Lee, H.-S.; Choi, S.-H. *Nanotechnology* **2004**, *15*, S660−S663.

consisted of a solution of glycine (192 mM) and Tris (25 mM) in 80%: 20% (v/v) water/methanol. The purified MPNs were dissolved in a 5% glycerol solution in Milli-Q water to a concentration of 4 mg $mL^{-1}$. This MPN solution was loaded on a 3 mm gel without lanes and eluted for 17 h at a constant voltage of 150 V to achieve separation. Parts of the gel containing each separated fraction were cut out and placed in Milli-Q water overnight. The gels lumps suspended in the solution were removed by filtration. MPNs were finally further purified by dialysis the same way as that described above.

**IR and VCD Spectroscopy.** Infrared (IR) and vibrational circular dichroism (VCD) spectra were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (<1800 $cm^{-1}$) put before the photoelastic modulator was used to enhance the signal/noise ratio. All solutions of *N*-isobutyryl-L/D-cysteine MPNs were prepared in NaOH/$D_2O$ solution. NaOH (6.5 mg in 0.8 mL $D_2O$) was added to completely deprotonate the carboxylic acid group. Solutions were prepared by dissolving 7 mg of MPNs in 50 $\mu$L of NaOH/$D_2O$ solution. A VCD spectrum of a racemic mixture of *N*-isobutyryl-L-cysteine MPNs and *N*-isobutyryl-D-cysteine MPNs was measured and served as the reference. This reference VCD spectrum was subtracted from the VCD spectra of the MPN enantiomers. All spectra were recorded at room temperature with a resolution of 8 $cm^{-1}$ in a cell equipped with $CaF_2$ windows and a 50 $\mu$m Teflon spacer. Both samples and reference were measured for 4 h in time slices of 1 h, corresponding to about 32 000 scans in total for samples and reference, respectively. The spectra are presented without smoothing or further data processing. More information about the experimental procedure can be found elsewhere.[31,32]

**Characterization of the Particles by UV−vis, CD, and NMR Spectroscopy.** $^1$H NMR spectra of the as-prepared particles were measured on a Brucker Avance 400 MHz spectrometer at room temperature. Solutions were prepared in $D_2O$ at a concentration of approximately 50 mg $mL^{-1}$. UV−vis and CD spectra, respectively, of the separated particles were collected on a Cary 300 and a Jasco 710 spectrometer, respectively, using a quartz cell of 1 cm path length and solutions of approximately 0.3 mg $mL^{-1}$ in $H_2O$.

**Transmission Electron Microscopy (TEM).** TEM images were recorded with a Philips C200 electron microscope operated at 200 kV. MPNs were made hydrophobic in order to avoid aggregation of particles.[33] An aqueous solution (5 mL) containing 1 mg of MPNs was set to pH 11 by addition of an aqueous solution of NaOH. To this solution was added 0.6 mM toluene solution (5 mL) of TOAB. The vigorous stirring of the mixture for 30 min resulted in complete transfer of colored MPNs from the aqueous to the organic phase. The latter was separated and concentrated to 500 $\mu$L. TEM sample was prepared by casting of a drop of the solution onto a carbon-coated copper grid.

**Density Functional Theory Calculations.** The adsorption of deprotonated *N*-isobutyryl-L-cysteine on $Au_8$ clusters was studied using Gaussian03.[34] For the gold atoms an effective core potential was used. The calculations were performed using the b3pw91[35,36] functional and an LanL2DZ basis set[37] for Au and a 6-31G(d,p) basis set[38] for all other atoms. Vibrational frequencies were scaled by a factor of 0.97. IR and VCD spectra were constructed from calculated dipole and rotational strengths assuming Lorentzian band shape with a half-width at half-maximum of 5 $cm^{-1}$.

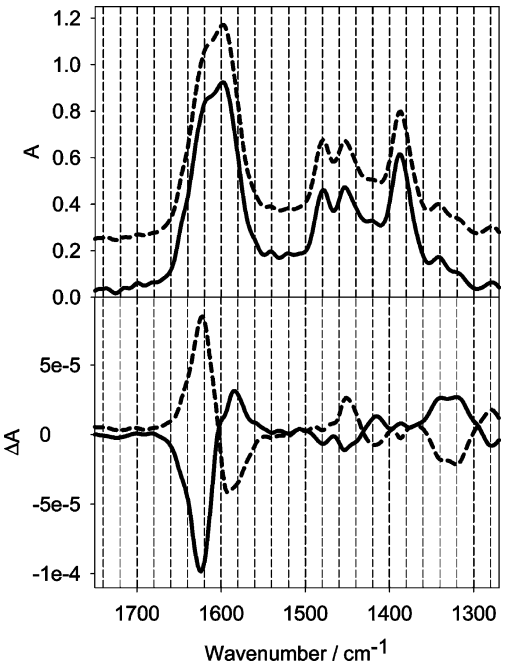



***Figure 1.*** Infrared (top) and VCD (bottom) spectra of *N*-isobutyryl-cysteine protected gold nanoparticles in NaOH/$D_2O$. Solutions were made from 7 mg of sample in 50 $\mu$L of solution. The dashed (solid) lines correspond to the spectra of the particles covered by the L-enantiomer (D-enantiomer). The IR spectrum of the particles covered with *N*-isobutyryl-L-cysteine was offset for clarity. See Experimental Section for more details.

## Results and Discussion

**TEM and NMR.** Transmission electron microscopy of the MPNs before gel electrophoresis separation reveals particle sizes around 2 nm and smaller (see Supporting Information). The $^1$H NMR spectrum (see Supporting Information) of unbound *N*-isobutyryl-cysteine displays four signals corresponding to hydrogen atoms which are not exchangeable with deuterium from $D_2O$. Their chemical shift is 1.1 ppm (dd, 6H), 2.6 ppm (m, 1H), 2.98 ppm (m, 2H), and 4.59 ppm (m, 1H), respectively, for the two methyl groups, the methine group in α position to the two methyls, the methylene, and the asymmetric methine, respectively. $^1$H NMR spectra of the *N*-isobutyryl-cysteine MPNs also show these four signals, which are however shifted and broadened compared to the free ligand. This observation shows that the ligand is intact and demonstrates the absence of the free ligand in solution. Line broadening is often observed in the NMR of MPNs and usually most pronounced for hydrogen atoms closest to the gold core.[39,40] In fact, the $^1$H NMR of gold *N*-isobutyryl-cysteine MPNs shows the largest line broadening for the methylene group in α position to the sulfur.

**IR and VCD Spectra of *N*-Isobutyryl-L-cysteine and *N*-Isobutyryl-D-cysteine Adsorbed on Gold MPNs.** The measured IR and VCD spectra of dissolved *N*-isobutyryl-D/L-cysteine MPNs are shown in Figure 1. Whereas the IR spectra

(31) Bürgi, T.; Vargas, A.; Baiker, A. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1596−1601.
(32) Bürgi, T.; Urakawa, U.; Behzadi, B.; Ernst, K.-H.; Baiker, A. *New. J. Chem.* **2004**, *28*, 332−334.
(33) Negishi, Y.; Tsukuda, T. *J. Am. Chem. Soc.* **2003**, *125*, 4046−4047.
(34) Frisch, M. J.; et al. *Gaussian 03*, rev. C.01 ed.; Gaussian, Inc.: Wallingford, CT, 2003.
(35) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(36) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671−6687.
(37) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283.
(38) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728.
(39) Terrill, R. H.; Postlethwaite, A.; Chen, C.; Poon, C.; Terzis, A.; Chen, A.; Hutchison, J. E.; Clark, M. R.; Wignall, G.; Londono, J. D.; Superfine, R.; Falvo, M.; Johnson, C. S.; Samulski, E. T.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 7.
(40) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17−30.

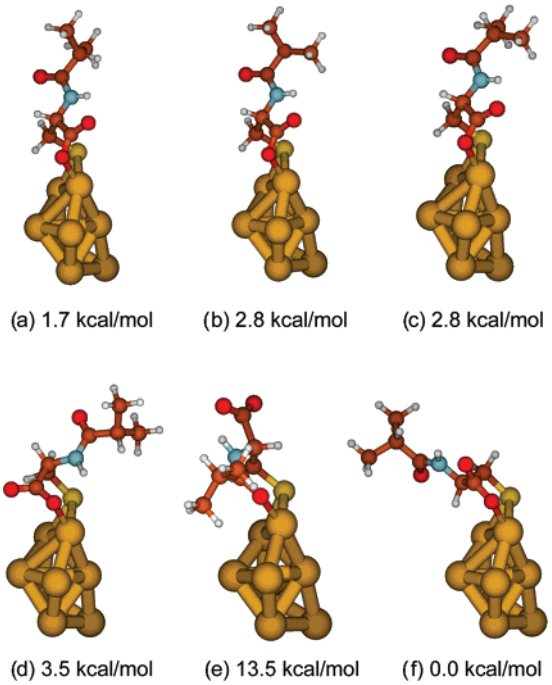



***Figure 2.*** Calculated conformers of deprotonated *N*-isobutyryl-L-cysteine on a $Au_8$ cluster. The numbers indicate the calculated relative stability with respect to the most stable conformer f. The calculations were performed at the B3PW91 level using a 6-31G(d,p) (LanL2DZ for Au) basis set.

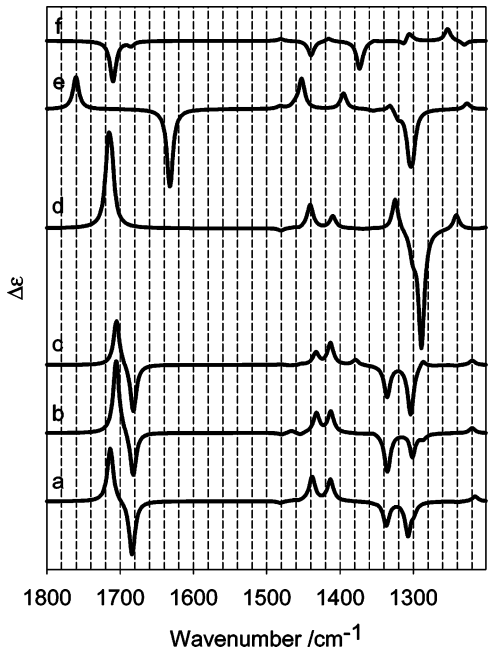



***Figure 3.*** Calculated VCD spectra for different conformers of *N*-isobutyryl-L-cysteine adsorbed on a $Au_8$ cluster. The letters correspond to the structures shown in Figure 2.

of the two MPN enantiomers are identical, the VCD spectra show a mirror image relationship. The slight deviation from the perfect mirror image relationship may be attributed primarily to noise. The largest deviation is observed for the $\nu_{as}(COO^-)$ band slightly below 1600 $cm^{-1}$. This band is the strongest in the spectrum. At this wavenumber the transmitted intensity is low, and consequently the noise, high. It should be noted that the measurements were performed on the as-prepared samples, which are not monodisperse. The appearance of relatively strong bands in the VCD spectra therefore indicates that the size of the particle has only a minor effect on the VCD and that the VCD is a local property of the individual adsorbed molecules. In contrast, no significant optical activity was observed in the UV−vis spectra for the as-prepared particles.

**Calculated VCD Spectra of *N*-Isobutyryl-L-cysteine MPNs.** VCD spectroscopy has been used in the past to determine the absolute configuration and to obtain structural information of small- and medium-sized molecules in solution.[31,32,41−44] To extract this information, VCD spectra for different conformations have to be calculated and compared with experiment. For adsorbed molecules on the nanoparticles the metal surface has to be considered in the calculations. We have chosen a $Au_8$ cluster to study the conformation of adsorbed deprotonated *N*-isobutyryl-L-cysteine. The cluster resembles a low energy conformer found recently for $Au_8$ using second-order perturbation theory (MP2) and coupled cluster methods (CCSD(T)).[45] Figure 2 shows some conformers of adsorbed deprotonated *N*-isobutyryl-L-cysteine that were found, and Figure 3 shows the corresponding calculated VCD spectra. The primary anchoring of the molecule to the cluster is through the sulfur atom in a bridge site, i.e., in between two Au atoms, in agreement with recent periodic density functional theory (DFT) calculations for cysteine[46] and methanethiol on Au(111).[47] The most important conformational degrees of freedom of the molecule are the rotations around the three single bonds involving the asymmetric C atom (two C−C bonds and one C−N bond, Chart 1). The amide part is rigid due to the strong preference of a trans arrangement of the C═O and N−H groups. Further conformational rigidity is provided by an intramolecular hydrogen bond between the N−H and the $COO^-$ groups. The isopropyl group can adopt several positions with respect to the rest of the molecule (compare conformations a−c in Figure 2). Energetically the one conformation where the C−H and C═O bonds are in trans arrangement (e.g., conformation a) is preferred over the other conformations (e.g., b and c). More importantly, we have noticed that the rotation of the isopropyl group has only a minor influence on the VCD spectra, as is obvious from Figure 3, spectra a−c. The reason for this finding emerging from the calculations is the weak VCD activity of the isopropyl group vibrations due to the local character of these modes (mainly $CH_3$).

Conformer a interacts with the $Au_8$ cluster via the sulfur atom and in addition with the carboxylate. The latter interaction leads to additional stability of the adsorbate complex. Note that in this conformation one oxygen atom of the $COO^-$ group interacts with the surface, whereas the other oxygen atom forms an intramolecular hydrogen bond with the N−H. In conformer d,

(41) Polavarapu, P. L.; Zhao, C.; Cholli, A.; Vernice, G. G. *J. Phys. Chem. B* **1999**, *103*, 6127−6132.
(42) Aamouche, A.; Devlin, F. J.; Stephens, P. J. *J. Am. Chem. Soc.* **2000**, *122*, 7358−7367.
(43) Freedman, T. B.; Cao, X.; Oliveira, R. V.; Cass, Q.; Nafie, L. A. *Chirality* **2003**, *15*, 196−200.
(44) Herse, C.; Bas, D.; Krebs, F. C.; Bürgi, T.; Weber, J.; Wesolowski, T.; Laursen, B. W.; Lacour, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3162−3166.
(45) Olson, R. M.; Varganov, S.; Gordon, M. S.; Metiu, H.; Chretien, S.; Piecuch, P.; Kowalski, K.; Kucharski, S. A.; Musial, M. *J. Am. Chem. Soc.* **2005**, *127*, 1049−1052.
(46) Di Felice, R.; Selloni, A.; Molinari, E. *J. Phys. Chem. B* **2003**, *107*, 1151−1156.
(47) Vargas, M. C.; Giannozzi, P.; Selloni, A.; Scoles, G. *J. Phys. Chem. B* **2001**, *105*, 9509−9513.

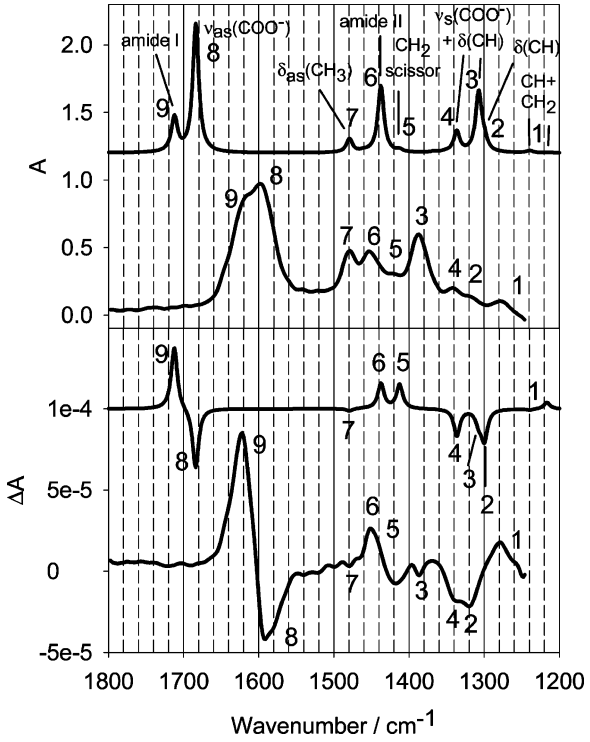



***Figure 4.*** Comparison between calculated (see Figure 3) and experimental IR and VCD spectra (see Figure 1) of *N*-isobutyryl-L-cysteine on gold. The calculated spectra are shown for conformer a in Figure 2. Corresponding bands are numbered and the assignment is given in the upper part of the figure.

one oxygen atom is responsible for both interactions (intramolecular hydrogen bonding and binding to the gold surface), whereas the other oxygen is free. This conformation is slightly less stable than conformer a. In conformer e the amide oxygen interacts with the surface, whereas the carboxylate does not, which leads to a considerable destabilization. In the most stable structure that was found, conformer f, the position of the asymmetric carbon atom within the seven-membered ring formed by the molecule and the $Au_8$ cluster (−Au−S−C−C−C−O−Au−) differs from its position in conformer a.

The VCD spectra for conformers a, d, e, and f differ considerably. For the most stable conformer f almost all prominent VCD bands are negative, in contrast to experiment. The VCD spectrum of conformer d exhibits two overlapping positive bands for the amide I and $\nu_{as}(COO^-)$ vibrations (calculated slightly above 1700 $cm^{-1}$) in contrast to experiment. Conformers a (and also the related conformers b and c) and e exhibit the correct sign for the amide I (positive) and $\nu_{as}(COO^-)$ (negative) vibrations. Based on the calculated energy conformer e is unlikely. The VCD spectrum of conformer a (also b and c) fits qualitatively well with experiment, when considering the assignment of vibrational bands as shown in Figure 4 and detailed below.

The highest energy vibrations in the considered frequency range belong to the amide I (1620 $cm^{-1}$, mode nr. 9 in Figure 4) and $\nu_{as}(COO^-)$ (1595 $cm^{-1}$, 8) modes. Consistent with the calculations for conformer a, the amide I vibration is less intense than the $\nu_{as}(COO^-)$ mode in the IR, whereas the former mode gains intensity (and even becomes more intense) relative to the latter in the VCD. Both modes are predicted at a too high frequency. This is primarily due to solvation effects, which strongly affects the frequency of these modes, and which are neglected in the calculations. The frequency of the $\nu_s(COO^-)$ mode observed at 1387 $cm^{-1}$ (nr. 3) is also strongly influenced by solvation. Consistent with the calculation this mode is only weakly VCD active (negative). The assignment of the $COO^-$ modes was confirmed by titration experiments. The $\delta_{as}(CH_3)$ modes above 1450 $cm^{-1}$ (nr. 7) are almost silent in the VCD both in experiment and calculations. The amide II mode (1450 $cm^{-1}$, nr. 6) is significantly positive in the calculations, in agreement with experiment. The calculations predict the $CH_2$ scissor mode (nr. 5) to be only weakly IR active but significantly positive in the VCD. Possibly this band is overlapping with the positive amide II mode (nr. 6) in the experimental VCD spectrum. A weakly negative band is observed slightly below the amide II band. Modes 4 and 2 contain C−H bending character and have negative intensity in both the experiment and the calculation. Between 1200 and 1300 $cm^{-1}$ the calculations predict a positive band with $CH_2$ (and some C−H) character in agreement with experiment. In summary, the VCD spectrum of conformer a is in qualitative agreement with experiment, which suggests that conformer a (and to a lesser extent conformers b and c) is the predominant conformation of *N*-isobutyryl-L-cysteine adsorbed on the gold nanoparticles.

From a purely energetic point of view and based only on the calculations conformer f should predominate. The VCD spectrum of the latter is however clearly not consistent with observation. It should also be noted that for *N*-acetyl-L-cysteine adsorbed on a $Au_4$ cluster the corresponding conformation a was slightly more stable than the corresponding conformer f,[27] which indicates that the relative energy of the different conformers may change slightly with structure and size of the gold cluster. Furthermore, the structural difference between the two ligands (*N*-acetyl-L-cysteine and *N*-isobutyryl-L-cysteine) is likely also influencing the relative stability of the corresponding conformers. In addition, lateral interaction between neighboring molecules, not considered in the calculation, may also influence the relative stability of the different conformers.

The conformation of *N*-isobutyryl-L-cysteine adsorbed on gold nanoparticles that we propose based on the VCD investigations resembles closely the one determined for *N*-acetyl-L-cysteine on gold surfaces based on attenuated total reflection infrared spectroscopy.[14,48] In the latter study the orientation of the molecule on the gold surface was determined from the orientation of the transition dipole moment for different vibrations. The proposed structure is also consistent with the structure of cysteine adsorbed on Cu surfaces as determined by reflection absorption spectroscopy.[49]

**Separation of Particle Compounds.** The *N*-isobutyryl-L-cysteine protected MPNs are charged and can therefore be separated according to their size and charge in a gel electrophoresis. Figure 5 shows a photograph of a gel after separation. Eight compounds could be separated and were numbered **1**−**8** according to increasing particle size. The UV−vis spectra of these compounds are given in Figure 6. TEM images of compounds **2** and **7** are given in the Supporting Information. Analysis of the TEM graphs reveals that compound **2** (the smallest compound observable by TEM) is characterized by a

(48) Bieri, M.; Bürgi, T. *J. Phys. Chem. B* **2005**, *109*, 22476−22485.
(49) Marti, M. E.; Methivier, C.; Pradier, C. M. *Langmuir* **2004**, *20*, 10223−10230.

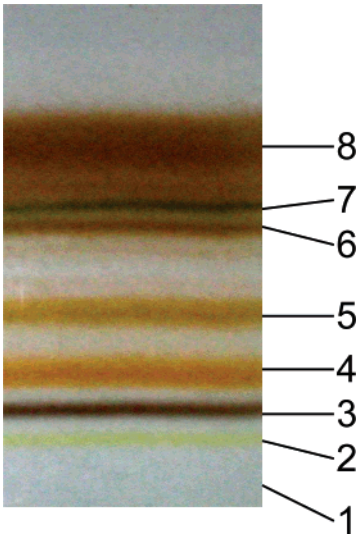



***Figure 5.*** Polyacrylamide gel electrophoresis (PAGE) separation of *N*-isobutyryl-L-cysteine protected gold particles. The separation was performed for 17 h at 150 V. The separated compounds are numbered from **1**−**8** according to their decreasing electrophoretic mobility. Compound **1** is only visible under UV irradiation.

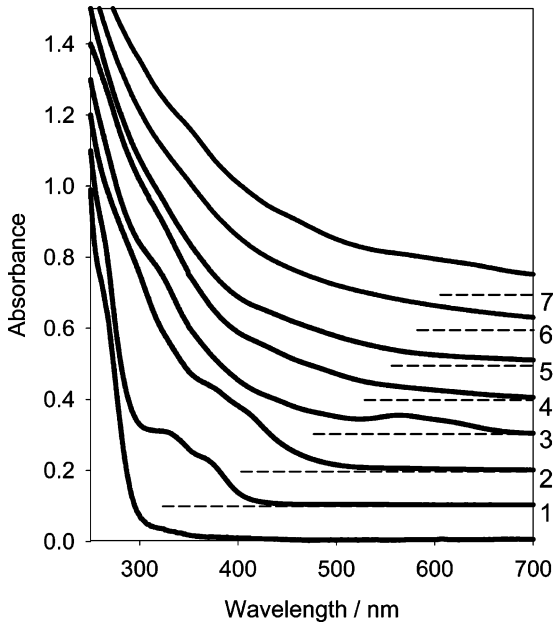



***Figure 6.*** UV−vis spectra of the separated compounds **1**−**8** (see Figure 5). Spectra are offset for clarity and normalized to 1 absorbance unit at 250 nm. The bottom spectrum corresponds to *N*-isobutyryl-L-cysteine (first derivative spectra are given in the Supporting Information).

particle size of about 0.7 nm, whereas compound **7** (the largest well-defined compound) is characterized by 1.3 nm particles. Compound **1** is invisible to the bare eye but becomes visible under UV irradiation. The color of the different compounds changes according to their size from yellow (**2**) to grayish (**3**) and orange (**4**) toward different tones of brown (**5**−**8**), which is a direct consequence of a quantum size effect. The separation is very good for compounds **1**−**5**, whereas band **8** is quite diffuse, which may indicate that several compounds with different compositions (number of gold atoms and thiol ligands) contribute to it. The appearance of discrete bands in the gel electrophoresis shows the presence of "magic number" compounds, i.e., the high relative abundance of compounds with a certain composition. It should be noted that the migration in the electrophoresis depends on both the size and the charge of the particles, the latter being dependent on the surface composition, i.e., the number of adsorbed ligands. In fact, it has been shown that gold clusters differing by only one adsorbed thiol ligand can be separated in a gel electrophoresis.[50] However, in this case the UV−vis spectra of the two compounds showed the same absorption onset. In contrast, the UV−vis spectra of our separated compounds reveal a red-shift with decreasing migration in the electrophoresis, which shows that the size of the metal core of the separated compounds is different.

Comparable separation of gold particles covered with thiols has been achieved in the past only for the gold L-glutathione system.[28,50−52] Schaaff and Whetten reported seven compounds,[28] whereas Tsukuda and co-workers reported up to nine separated compounds for the same system (and some less for homoglutathione).[50] Preparation and separation of other water-soluble gold thiol MPNs have been reported but resulted in considerably less isolated compounds.[53] Very recently three different compounds were separated for gold particles coated with penicillamine.[29] 4-Mercaptobenzoic acid was reported to yield two separated bands in a gel electrophoresis (PAGE), whereas numerous other water soluble passivated gold particles did not show discrete bands.[53]

**UV−vis Spectra.** Figure 6 shows the UV−vis spectra of the compounds isolated from the gel and after purification by dialysis. The absorption spectra exhibit considerable structure, in particular for the smaller compounds (bands **1**−**3**), which is even more evident from the first derivative of the spectra (see Supporting Information). The UV−vis spectra reveal that the compounds exhibit well quantized electronic structures. In addition, an absorption onset is observed, which shifts from slightly above 400 nm for compound **1** to higher wavelengths as the size of the compound increases. For compounds **1**−**3** two distinct bands are observed after the absorption onset. Similar UV−vis spectra were reported for gold particles passivated by L-glutathione (*γ-glu-cys-gly*).[50] Figure 7 shows a comparison between the first three compounds isolated for L-glutathione covered particles (from ref 50) and for *N*-isobutyryl-L-cysteine covered particles. The similarity is striking. From this comparison we conclude that the absorption spectra are basically determined by the metal core of the particle, as the ligands (L-glutathione and *N*-isobutyryl-L-cysteine) are different. The comparison furthermore indicates that the corresponding particles have the same core size and similar core structures, since the electronic structure of such small metal particles is both sensitive to size and structure.[54]

Using electrospray ionization (ESI) mass spectrometry Tsukuda and co-workers analyzed the mass of separated gold−L-glutathione compounds.[50] From their results and the comparison in Figure 7 it is concluded that the gold−*N*-isobutyryl-cysteine compounds **1**, **2**, and **3** contain 10 (−12), 15, and 18 gold atoms, respectively. Tsukuda and co-workers concluded, based on

(50) Negishi, Y.; Nobusada, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 5261−5270.
(51) Schaaff, T. G.; Knight, G.; Shafigullin, M. N.; Borkman, R. F.; Whetten, R. L. *J. Phys. Chem. B* **1998**, *102*, 10643−10646.
(52) Negishi, Y.; Takasugi, Y.; Sato, S.; Yao, H.; Kimura, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2004**, *126*, 6518−6519.
(53) Ackerson, C. J.; Jadzinsky, P. D.; Kornberg, R. D. *J. Am. Chem. Soc.* **2005**, *127*, 6550−6551.
(54) Li, X.; Kiran, B.; Li, J.; Zhai, H.-J.; Wang, L.-S. *Angew. Chem, Int. Ed.* **2002**, *41*, 4786−4789.

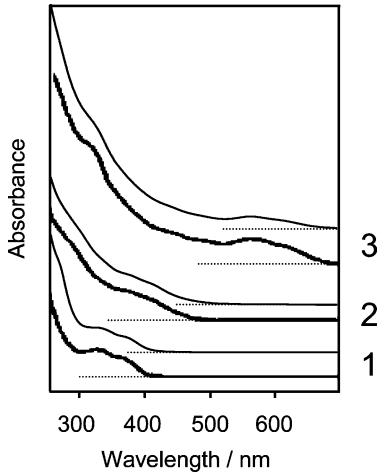



***Figure 7.*** Comparison between UV−vis spectra of separated gold *N*-isobutyryl-L-cysteine compounds **1**−**3** (see Figure 5) and corresponding L-glutathione compounds reported in ref 50 (with permission from the American Chemical Society).

X-ray photoelectron spectroscopy and photoemission spectroscopy, that even the smallest compound (10−12 gold atoms) is clearly distinguishable from a Au(I)-SR polymer.[50]

Based on a density functional theory (DFT) calculation on $[Au_{13}(SCH_3)_8]^{3+}$ the two characteristic bands above the absorption onset observed for small gold *N*-isobutyryl-cysteine (L-glutathione) compounds (see Figures 6 and 7) may be assigned to electronic transitions from the Au 6s to the Au 6s and Au 6s/6p orbitals corresponding to "intraband" transition in the bulk metal.[55] On the other hand the structure in the absorption spectra at around 300 nm and below may correspond to transitions from Au 5d to Au 6s/6p orbitals, corresponding to "interband" transitions in the bulk metal. According to these calculations some orbitals involved in the described electronic transitions contain appreciable sulfur 3p and 3s character. It is therefore expected that a different number of ligands or a different arrangement of the same number of ligands on the metal particle affect the electronic transitions and therefore the absorption spectrum. Indeed for the gold−L-glutathione particles ESI mass spectrometry indicated that two isolated compounds differed by only one ligand.[50] More precisely, compounds **4** and **5** reported by Tsukuda and co-workers were assigned to $Au_{22}$ particles containing 16 and 17 L-glutathione ligands, respectively. The corresponding UV−vis spectra showed appreciable differences. This observation is furthermore supported by electronic structure calculations on small gold clusters.[56] The latter calculations reveal that the adsorption of thiols modifies the frontier orbitals and leads to considerable deformation of the metal core.

The discussion in the previous paragraph and the striking similarity between the UV−vis spectra of the L-glutathione and N-isobutyryl-L-cysteine passivated gold particles (Figure 7) indicates that for compounds **1**−**3** the number and arrangement of thiols on the cluster is the same independent of the nature of the thiol. This is in accord with the general knowledge that the bonding of thiols on gold is determined by the strong affinity between sulfur and gold. However, this finding is somewhat surprising given the fact that the two thiols considered here (L-glutathione and *N*-acetyl-L-cysteine) have rather different sizes, which should translate into a different number of surface gold atoms occupied by one adsorbed molecule. This argument is certainly valid for flat surfaces, but the size of the thiol becomes less important for nanoparticles with their highly curved convex surfaces. It should be noted that the above discussion addresses the comparison between separated particles of the same very small size, which should not be confused with the mean particle size. The latter is normally shifted to a smaller size when using larger thiols.[57]

It has been noted before for the gold−L-glutathione system that the number $n$ of gold atoms in the different compounds ("magic numbers") does not correspond to the closing of geometrical (13, 20, 28, 38...) nor electronic shells (8, 18, 20...).[50] Another possibility that was considered is the completion of the ligand shell, which stabilizes certain sizes of the gold particles. The results discussed above indicate that this argument may not be valid, as the size of the thiol ligand seems to have no influence on the number of thiols adsorbed on the corresponding gold compounds **1**−**3**. Furthermore, the size of the thiol ligand (steric demand) was argued to favor the selective production of very small particles and to render the latter more stable.[51] Our work shows that gold particles with the same size can be obtained using a considerably smaller ligand. In addition, the *N*-isobutyryl-cysteine protected gold particles were found to be at least as stable as similar L-glutathione protected gold particles prepared and stored under identical conditions. After storing the nanoparticles for several months at ambient conditions the electrophoresis hardly changed, whereas noticeable changes were observed for L-glutathione MPNs, as was already reported before.[50]

**Optical Activity in the UV−vis.** Figure 8 shows a comparison between the UV−vis and CD spectra of compounds **2**−**4** covered with the two enantiomers of *N*-isobutyryl-cysteine. The corresponding spectra of *N*-isobutyryl-cysteine exhibit optical activity only below 300 nm (see Supporting Information). The optical activity of the other compounds was weaker. The CD spectra of the particles covered with the two enantiomers show (nearly) a mirror image relationship, whereas the corresponding UV−vis spectra are basically identical. However, the mirror image relationship in the CD spectra is not perfect particularly for compounds **3** and **4**.

To the best of our knowledge the preparation, separation, and CD spectra of gold particles covered with enantiomers of thiols were reported only once before (for penicillamine protected gold particles).[29] The CD spectra of the particles covered with the enantiomers of penicillamine showed also a (nearly) mirror image relationship. One possible explanation for the slight deviation from the perfect mirror image relationship is that the isolated bands in the gel electrophoresis still contain two or more compounds with the same mobility and composition but with slightly different structures. The varying relative amount of these subcompounds obtained in different synthesis batches (different enantiomers) could cause the slight deviation from the perfect mirror image relationship in the CD spectra.

The strongest optical activity is observed for compound **2**. The anisotropy factors (see Supporting Information) have the same order of magnitude as those reported for L-glutathione MPNs and penicillamine MPNs. For the penicillamine protected

(55) Nobusada, K. *J. Phys. Chem. B* **2004**, *108*, 11904−11908.
(56) Garzon, I. L.; Reyes-Nava, J. A.; Rodriguez-Hernandez, J. I.; Sigal, I.; Beltran, M. R.; Michaelian, K. *Phys. Rev. B* **2002**, *66*, 73403.
(57) Yonezawa, T.; Yasui, K.; Kimizuka, N. *Langmuir* **2001**, *17*, 271−273.

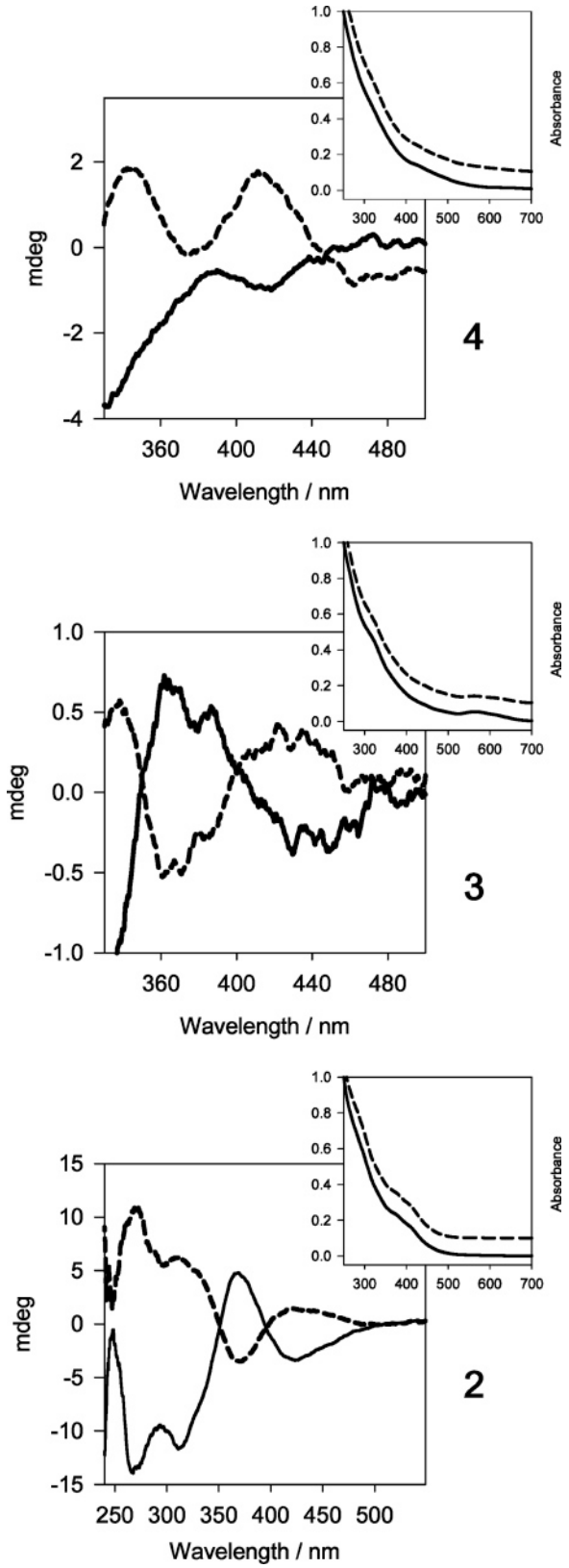



***Figure 8.*** CD and UV−vis spectra of separated compounds **2**−**4** of gold particles covered with *N*-isobutyryl-L-cysteine (dashed) and *N*-isobutyryl-D-cysteine (solid line). The UV−vis spectra were scaled to 1 absorbance unit at 250 nm.

gold particles the anisotropy factors decreased with increasing particle size.[29] Our findings do not contradict this tendency, although it seems less clear for the *N*-isobutyryl-L-cysteine case (only weak optical activity for compound **1**, relatively weak anisotropy factor for compound **3**). This tendency follows the surface-to-volume ratio of the particles and may thus point toward a surface effect as the origin for the optical activity (see discussion below).

It is important to note here that all the gold particles which were separated by a gel electrophoresis and for which optical activity has been reported in the UV−vis (L-glutathione,[28] penicillamine,[29] and *N*-isobutyryl-L-cysteine) are relatively small. The metal core diameters of these particles are 1 nm or below, with the exception of one penicillamine gold particle showing only relatively weak optical activity, which had a particle diameter (according to SAXS) larger than 1 nm. In contrast, optical activity was also reported for considerably larger silver particles (23.5 nm). However, these particles were not separated, and it cannot be excluded that the observed optical activity is due to a fraction of small particles formed during the addition of the thiol to the silver colloids.[30] Another explanation for the tendency of decreasing optical activity with increasing particle size is simply the increased configurational space for larger particles (larger number of gold atoms and ligands) and thus the increased probability of multiple energy minima on the potential energy surface. An increasing number of conformers leads to a decreased observable optical activity as positive and negative bands of different conformers average out.

Considering all the available CD spectra of gold particles protected with chiral thiols (L-glutathione,[28] penicillamine,[29] and *N*-isobutyryl-L-cysteine) another trend is remarkable. The CD spectra tend to be preferentially either positive or negative. In the L-glutathione case the CD is dominated by positive bands.[28] For the penicillamine protected gold particles most of the bands in the CD are positive in the for the L-enantiomer.[29] For the two larger compounds almost only positive bands were observed. For the *N*-isobutyryl-L-cysteine protected gold particles investigated here this tendency is also observed, with a more positive intensity in the CD spectra for the L-enantiomer. The sign of the predominant intensity in the CD spectra of the chiral particles (positive or negative) correlates with the absolute configuration of the thiol, penicillamine, or cysteine (for *N*-acetyl-L-cysteine and L-glutathione). Due to the limited data available today, the described trend may be on one hand only by chance but may on the other hand point toward the origin of the optical activity in these compounds.

**Origin of Optical Activity in the UV−vis.** The origin of the observed optical activity in the small gold particles protected with chiral thiols has been discussed before.[28,29] The principal possibilities are the same as those described for flat metal surfaces in the Introduction. The key question remains whether the metal particle is intrinsically chiral or whether the optical activity is induced by the chiral environment.[58] The first possibility has support from theoretical calculations which indicate that small metal particles such as $Au_{28}$ prefer low symmetry chiral over high-symmetry nonchiral structures.[56,59] Several mechanisms for the arising optical activity were proposed for nonchiral metal particles in a chiral environment. These include the chiral arrangement of the ligands and the

(58) Goldsmith, M.-R.; George, C. B.; Zuber, G.; Naaman, R.; H., W. D.; Wipf, P.; Beratan, D. N. *Phys. Chem. Chem. Phys.* **2006**, *8*, 63−67.
(59) Garzon, I. L.; Beltran, M. R.; Gonzalez, C.; Gutierrez-Gonzalez, I.; Michaelian, K.; Reyes-Nava, J. A.; Rodriguez-Hernandez, J. I. *Eur. Phys. J. D* **2003**, *24*, 105−109.

influence of the asymmetric centers of the chiral ligands (through space or through bonds) on the electronic structure of the metal. Likely some of these effects are not easily separable for the gold compounds prepared in this study. For example, if the thiols indeed adsorb in a chiral arrangement, it is very likely that the gold particle itself is distorted toward a chiral structure because the adsorption of a thiol leads to a distortion of the surface gold atoms.[59] Even adsorption of single chiral molecules can lead to a chiral "footprint" on a nonchiral surface, i.e., the relaxation of the surfaces atoms involved in the adsorbate complex toward a chiral structure, as was shown for tartaric acid adsorption on Ni surfaces.[15] It is hard to imagine that the thiol gold interaction, i.e., a one point interaction, leads to a chiral "footprint". However, the VCD investigation indicates that the carboxyl group is also interacting with the gold particle, which may induce a chiral "footprint" on the surface of the particle and lead to the observed optical activity. A possible model of a chiral "footprint" induced by a double interaction is given in the Supporting Information. This possibility is consistent with the trend that the optical activity is decreasing with particle size. In addition, all the thiols that were reported to induce optical activity in gold and silver particles, penicillamine,[29,30] L-glutathione,[28,30] cysteine,[30] and *N*-isobutyryl-cysteine contain an acid group, which can interact with the metal surface in addition to the thiol. Such double interactions have indeed been documented in the past.[27,48,49,60,61] Furthermore, it was reported for Ag particles that the adsorption of cysteine (penicillamine and L-glutathione) induced optical activity. However, when the acid group was blocked in cysteine methyl ester no optical activity was observed,[30] which further supports the idea that the acid group plays an important role for the induction of optical activity in the metal-based transitions, through imparting a chiral "footprint" onto the metal particle surface. The idea that an adsorbed thiol can considerably distort the structure of the underlying small metal particle is not so astonishing. In fact, very recently several papers have appeared where the influence of thiol adsorption on the structure of small particles has been shown.[62,63] The formation of a chiral "footprint" on a particle induced by a chiral thiol seems thus also plausible.

## Conclusions

Small gold particles protected with *N*-isobutyryl-D-cysteine and *N*-isobutyryl-L-cysteine, respectively, were prepared, and their optical activity in the infrared and UV−vis was investigated. The vibrational circular dichroism (VCD) spectra of the as-prepared samples show a mirror image relationship for particles covered with the two enantiomers. Density functional theory calculations reveal that the VCD spectra strongly depend on the conformation of the adsorbed *N*-isobutyryl-cysteine. The VCD spectra are consistent with a conformation where the carboxylate interacts with the gold particle in addition to the thiol, and the study furthermore demonstrates the power of VCD spectroscopy for structure determination of molecules adsorbed on nanoparticles.

The as-prepared nanoparticles consist of few distinct compounds with well-defined compositions, i.e., gold atoms and ligands, which can be separated according to their size and charge in a gel electrophoresis. The UV−vis spectra of the separated compounds reveal the well-quantized electronic structure of these particles and a systematic red-shift of the absorption onset with increasing particle size, which is also evident from the color of the individual compounds. The UV−vis spectra of some of the separated compounds are astonishingly similar to the UV−vis spectra of analogous particles covered with L-glutathione indicating the same composition, i.e., number of Au atoms and thiol ligands. Thus, for these small particles the composition is independent of the thiol, i.e., L-glutathione and *N*-isobutyryl-cysteine, respectively, despite the fact that the sizes of the two thiols are largely different. Some of the separated compounds reveal large optical activities. Based on the present findings and the information available on optically active gold nanoparticles the origin of the optical activity is discussed. Up to now, all the thiols leading to optically active nanoparticles contain at least one carboxylic acid group. The VCD investigation indicates that the carboxylic acid group interacts with the gold particle, and it is proposed that this "two point interaction" leads to a chiral "footprint" on the particle surface, which is the origin of the observed optical activity.

**Acknowledgment.** Financial support by the Swiss National Science Foundation and grants of computer time by the Swiss National Supercomputer Centre (Manno) are kindly acknowledged. We thank Massoud Dadras, Institute of Microtechnology, for TEM measurements.

**Supporting Information Available:** Complete ref 34, first derivative of UV−vis spectra of compounds **1**−**7**, UV−vis and CD spectra of *N*-isobutyryl-L-cysteine and *N*-isobutyryl-D-cysteine, 400 MHz $^1$H NMR spectra of *N*-isobutyryl-L-cysteine MPNs, transmission electron microscope (TEM) images of *N*-isobutyryl-L-cysteine MPNs before separation, TEM images of compounds **2** and **7**, and anisotropy factors for compounds **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA058717F

(60) Bieri, M.; Bürgi, T. *Langmuir* **2005**, *21*, 1354−1363.
(61) Bieri, M.; Bürgi, T. *Phys. Chem. Chem. Phys.* **2006**, *8*, 513−520.
(62) Nunokawa, K.; Onaka, S.; Ito, M.; Horibe, M.; Yonezawa, T.; Nishihara, H.; Ozeki, T.; Chiba, H.; Watase, S.; Nakamoto, M. *J. Organomet. Chem.* **2006**, *691*, 638−642.
(63) Negishi, Y.; Takasugi, Y.; Sato, S.; Yao, H.; Kimura, K.; Tsukuda, T. *J. Phys. Chem. B* **2006**, *110*, 12218−12221.